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“True” Inorganic Heterocycles: Structures and Stability of Group 13–15 Analogues of Benzene and Their Dimers

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Group 13–15 inorganic analogues of benzene, $[HMYH]_3$ (M = B, Al, Ga; Y = N, P, As), mixed heterocycles of the type $[BAlGaNPAs]H_6$ and their dimers have been theoretically examined at the B3LYP/TZVP level of theory. Six different isomers have been structurally characterized for the mixed compounds $[BAlGaNPAs]H_6$. B–N bonding strongly (about ~90–100 kJ mol^{-1}) stabilizes the mixed heterocycles, followed by the preference of the Al–N bonded structures over Ga–N bonded (~30–40 kJ mol^{-1}), while B–P bonding is slightly (5–10 kJ mol^{-1}) more favorable compared to B–As. Thus, the $\overline{\text{B–N–Al–As–Ga–P}}$ bonding pattern is predicted to be the most stable, followed by the $\overline{\text{B–N–Al–P–Ga–As}}$ core. Processes of $[HMYH]_3$ formation from donor–acceptor complexes H_3MYH_3 are predicted to be thermodynamically favorable for all MY combinations. Dimerization reactions of the coordinationally unsaturated $[HMYH]_3$ heterocycles yielding hexamer clusters $[HMYH]_6$ are found to be *exothermic*, with the exception of borazine, for which, as for benzene, dimerization is strongly *endothermic* due to the aromaticity of C_6H_6 and $[HBNH]_3$. Despite the high endothermicity of $[HBNH]_3$ dimerization, the B–N bond formation is the driving force of the dimerization of mixed species $[BAlGaNPAs]H_6$. The dimerization enthalpies of $[BAlGaNPAs]H_6$ may be both exo- and endothermic, depending on the bonding pattern of the isomers. A complete set of mean MY bond energies in four- and six-membered cycles of $[HMYH]_6$ was derived. The MY energies were found to be transferable quantities and may serve for a qualitative prediction of the relative stability of different isomers of mixed cluster compounds. $[BAlGaNPAs]_2H_{12}$ clusters are promising synthetic targets, they are expected to serve as single-source precursors for the stoichiometry-controlled CVD processes of the group 13–15 composites. A strategy of their synthesis and the most suitable starting systems have been also predicted.

1. Introduction

Group 13−15 composites are prospective materials for the microelectronic industry. Mixed nitrides $Al_xGa_yIn_zN$ serve as light emitting diodes (blue, red, and green) for display applications.[1] Some materials, such as $Tl_yIn_yGa_zP$ and $Tl_yIn_yGa_zAs$ are predicted to have temperature-independent properties, which makes them promising materials for the fiber optic data transition systems.[2] Chemical vapor deposition(CVD) processes are widely used for production of binary group 13−15 materials.[3] In principle, using different group 13 and 15 precursors, a composite material may be deposited, for example, for $Al_xGa_{1-x}N_yP_{1-y}$:

$$x\mathrm{Al(CH_3)_3}\ (g) + (1-x)\mathrm{Ga(CH_3)_3}\ (g) + y\mathrm{NH_3}\ (g) + (1-y)\mathrm{PH_3}\ (g) = \mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{N}_y\mathrm{P}_{1-y}\ (s) + 3\mathrm{CH_4}\ (g)$$

However, the control of the composition of the film (x and y) obtained in such reactions is yet to be achieved by

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chemists.[4] Alternatively, single-source precursors which contain all elements in an already precombined state may provide an excellent solution for the stoichiometry control of the film composition. Ring and cluster compounds of group 13−15 elements appear to be the compounds of choice. During the past decades the preparative chemistry of rings and clusters $[R_2MYR'_2]_m$ and $[RMYR']_n$ (M = group 13 element; Y = group 15 element) has improved dramatically.[5−7] It was found, that for the organometallic analogues the oligomerization degree m, n ($m = 2, 3$; $n = 2-8, 10, 15, 16$) depends on the bulkiness of the substituents R,R′. Many new organometallic and several inorganic compounds have been synthesized during the past decade which served as precursors for group 13−15 materials. In fact, rings and clusters with Al−N[8] and Ga−N[9] cores have been extensively studied experimentally and their ability to serve as single-source precursors toward deposition of AlN and GaN has been demonstrated. Recently, mixed dimeric cyclic compounds $[R_2GaYY'R'_2]_2$ with Ga_2PAs, Ga_2PSb, and Ga_2AsSb cores have been used as precursors toward nanocrystalline gallium-poor GaP_xAs_{1-x}, GaP_xSb_{1-x}, and $GaAs_xSb_{1-x}$.[10] On the other hand, Ga−As-containing trimeric rings $[R_2GaAsR'_2]_3$ were found ineffective for the GaAs deposition due to As loss.[11] A theoretical approach toward the single-source precursor concept based on modeling of gas-phase reactions has been recently presented.[12] It was shown, that the formation of dimeric ring species $[X_2MYH_2]_2$ in the gas phase (M = Al, Ga, In; Y = N, P, As; X = H, F, Cl, Br, I) is thermodynamically most favorable for X = H. The stability of the MY bond in the gas phase will result in preserving the 13/15 ratio during the deposition process.

However, as far as we know, no precursors containing more than two different group 13 or 15 elements have been investigated experimentally or theoretically. In contrast to the dimeric rings $[X_2MYH_2]_2$, oligomeric $[XMYH]_n$ rings and clusters offer much greater variety in making different compositions of group 13 and 15 elements. In the present report the simplest models of mixed $[XMYH]_n$ clusters (X = H; $n = 3, 6$) are considered. Trimeric “true inorganic heterocycles” $[BAlGaNPAs]H_6$ containing all different group 13 and 15 elements in the ring, and their dimers $[BAlGaNPAs]_2H_{12}$, are theoretically investigated for the first time. The structures, stability, and thermodynamic properties of the inorganic analogues of benzene $[HMYH]_3$ (M = B, Al, Ga; Y = N, P, As) and their dimers $[HMYH]_6$ are also considered for comparison.

To describe larger $[HMYH]_n$ associates with a variety of group 13 and 15 elements, a bond energy model based on the transferability of the MY bond energies in cluster compounds may be helpful. The validity of the bond energy model was demonstrated by Yang et al.[13]for the dimeric rings $[H_2(M,M')(Y,Y')H_2]_2$ (M = Al, Ga, In; Y = P, As). Mean MY bond energies for the ring and cluster compounds $[HMYH]_{3,6}$ will be given in the present work, and the transferability of the derived quantities will be tested.

First we will present structures and relative energies of mixed $[BAlGaNPAs]H_6$ rings and we will compare them to inorganic benzenes $[HMYH]_3$. Then we consider the thermodynamics of the dimerization processes and derive mean MY bond energies for the $[HMYH]_3$ and $[HMYH]_6$ species. At last, the transferability of the MY bond energies will be tested for dimerization reactions of mixed $[BAlGaNPAs]H_6$ rings yielding $[BAlGaNPAs]_2H_{12}$ clusters.

2. Computational Details

All structures were fully optimized and verified with subsequent vibrational analysis to be minima on the potencial energy surface (PES). Density functional theory in the form of the hybrid B3LYP functional[14] was used together with the full-electron triple-ζ quality TZV basis set of Ahlrichs, augmented by d-type polarization functions (TZVP). For H a standard 6-311G** basis set was employed.[15] In some cases the performance of the unaugmented TZV basis was also tested. The Gaussian 98 suite of programs[16] was used throughout. The basis set superposition error (BSSE) correction was evaluated by the counterpoise method.[17]

The B3LYP functional usually gives good prediction of the thermodynamic properties for group 13−15 elements. The average

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Table 1. Comparison between Calculated and Experimental Thermodynamic Characteristics[a]

process	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	method	reference
$C_2H_6 = (1/3)C_6H_6 + 2H_2$	129.7	122.1	B3LYP/TZV	this work
	113.4	122.4	B3LYP/TZVP	this work
	111.4	121.5	exptl	19
$BH_3 + NH_3 = (1/3)[HBNH]_3 + 2H_2$	−200.0	−22.2	B3LYP/TZV	this work
	−213.8	−21.4	B3LYP/TZVP	this work
	−230.8	−23.0	exptl	19

[a] Standard reaction enthalpies $\Delta H^0_{(298)}$ are in kJ mol^{-1}, standard reaction entropies $\Delta S^0_{(298)}$ are in J mol^{-1} K^{-1}.

difference between experimental and theoretical dissociation enthalpies of the X_3MNH_3 donor−acceptor complexes was found to be 7 kJ mol^{-1} (M = Al, Ga, In; X = Cl, Br).[18] Computed thermodynamic properties of the reaction of formation of benzene and borazine (the only experimentally known substances among the considered $[HMYH]_3$ cycles) are compared with experimental data in Table 1. As can be seen, inclusion of the polarization functions produces much better agreement with experimental values for standard enthalpies. For the B3LYP/TZVP level of theory, the average error for standard enthalpy is 9 kJ mol^{-1}, for standard entropy it is 1.3 J mol K^{-1}. The error in standard enthalpy for the heterocyclic borazine (17 kJ mol^{-1}) is much larger compared to that of benzene (2 kJ mol^{-1}). It is more likely that the errors for the other heterocycles will be similar to that of borazine. Predicted standard entropies are in excellent agreement with experiment both for benzene and borazine.

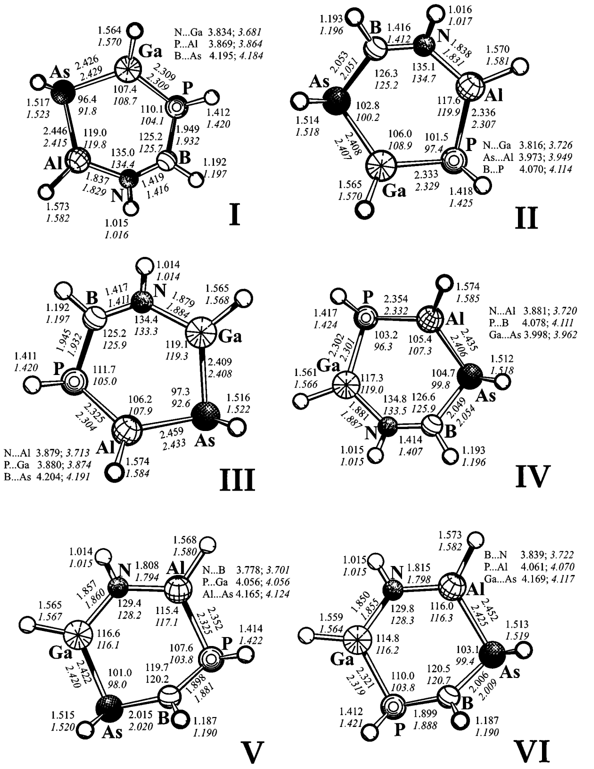

Figure 1. Optimized structures of six isomers of "inorganic benzene" $[BAlGaNPAs]H_6$ (top view). Bond distances in angstroms, bond angles in degrees. B3LYP/TZV (normal text) and B3LYP/TZVP levels of theory (in italics).

Table 2. Bonding Pattern and Relative Energies E^{rel} (kJ mol^{-1}) of the $[BAlGaNPAs]H_6$ Isomers, the MY Bonding in the Most Suitable Precursor System for Their Synthesis

isomer	bonding pattern	E^{rel} B3LYP/TZV	E^{rel} B3LYP/TZVP	MY bonding in precursor system
I	BNAlAsGaP	0	0	AlN, GaAs, BP
II	BNAlPGaAs	5.3	13.2	BAs, AlN, GaP
III	BNGaAsAlP	30.9	39.3	BP, GaN, AlAs
IV	BNGaPAlAs	40.0	55.1	BAs, AlP, GaN
V	BPAlNGaAs	89.6	99.4	BAs, AlP, GaN
VI	BPGaNAlAs	92.4	102.8	BP, AlAs, GaN

3. Results and Discussion

A. Structures and Relative Energies. For the inorganic analogues of benzene with $[BAlGaNPAs]H_6$ composition, six spatial isomers with different group 13−15 bonding pattern in the ring are possible. The optimized structures and numbering of the isomers are presented in Figure 1. All isomers have nonplanar structures (C_1 symmetry). The nitrogen and group 13 centers exhibit a tendency toward planar coordination, while the P and As centers are pyramidal. The TZV and TZVP basis sets have similar performances in bond lengths (with the exception of the Al−P and Al−As bonds, which are up to 0.03 Å shorter at TZVP). The major difference was found in the angles around P and As centers: the predicted values at B3LYP/TZVP are up to 5° smaller compared to B3LYP/TZV. Energies relative to the most stable isomer **I** are given in Table 2.

All six isomers may be divided with regard to their relative stability into three groups. The less stable (by 90−100 kJ mol^{-1}) species are isomers **V** and **VI,** which lack B−N bonding. Therefore, we conclude that a B−N bond is essential for the stabilization of the ring. Within four B−N bonded structures, the most stable ones are two structures with Al−N bonds (isomers **I** and **II**), while the Ga−N bonded structures **III** and **IV** are 30−50 kJ mol^{-1} higher in energy. Very minor contributions arise from B−P versus B−As bonding, structures which possess B−P bond are slightly (5−10 kJ mol^{-1}) more stable compared to B−As bonded, as follows from the energies of structures **I** and **II**, **III** and **IV**. Al−P bonding is about 2−3 kJ mol^{-1} more favorable compared to Ga−P (isomers **V** and **VI**). We predict that, among all species, isomers **I** and **II** with B−N−Al−As−Ga−P and B−N−Al−P−Ga−As bonding patterns, respectively, are most stable and may be attractive targets for synthesis.

It is of interest to compare the data about the stability of the mixed rings toward “homoatomic” trimeric rings $[HMYH]_3$, formed by only one group 13 and group 15 element (M = B, Al, Ga; Y = N, P, As). To this end, all

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Table 3. Geometric Parameters of $[HMYH]_3$ Compounds and Thermodynamic Characteristics of the Reaction of Their Formation from the Donor−Acceptor Complexes: $H_3MYH_3 = (1/3)[HMYH]_3 + 2H_2$ Predicted at B3LYP/TZVP[a]

M,Y	point group	R(M−Y)	R(H−M)	R(Y−H)	−MYM	−YMY	$\Delta H^0_{(298)}$	$\Delta S^0_{(298)}$	$\Delta G^0_{(298)}$
CC	D_{6h}	1.392	1.084	1.084	120.0	120.0	113.4	122.4	76.9
BN	D_{3h}	1.431	1.193	1.008	123.0	117.0	−104.4	119.8	−140.1
BP	C_{3v}	1.856	1.187	1.408	119.0	117.0	32.9	112.5	−0.6
BAs	C_{3v}	1.989	1.188	1.510	108.1	119.5	29.5	105.4	−1.8
AlN	D_{3h}	1.802	1.581	1.013	125.5	114.5	−50.7	111.6	−84.0
AlP	C_{3v}	2.317	1.583	1.424	100.7	117.0	−35.4	107.7	−67.5
AlAs	C_{3v}	2.423	1.585	1.523	96.1	117.5	−61.2	106.9	−93.1
GaN	D_{3h}	1.849	1.560	1.012	126.8	113.2	12.1	108.3	−20.2
GaP	C_{3v}	2.323	1.570	1.424	100.3	117.1	−39.8	104.4	−70.9
GaAs	C_{3v}	2.428	1.574	1.523	96.3	117.7	−69.7	105.4	−101.1

[a] Bond distances are in angstroms, bond angles in degrees, standard enthalpies $\Delta H^0_{(298)}$ and standard Gibbs energies $\Delta G^0_{(298)}$ in kJ mol^{-1} and standard entropies $\Delta S^0_{(298)}$ in J mol^{-1} K^{-1}.

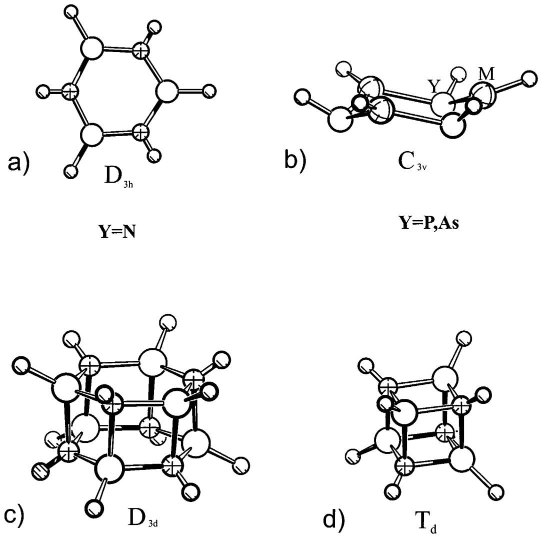

Figure 2. General structures of nitrogen-containing trimers $[HMNH]_3$ (a), P and As trimers $[HM(P,As)H]_3$ (b), $[HMYH]_6$ hexamers (c), and $[HMYH]_4$ cubic tetramers (d).

nine inorganic analogues of benzene $[HMYH]_3$ have been optimized. The calculated structural parameters are given in Table 3. In agreement with previous theoretical assessments,[20] nitrogen-containing molecules are planar with D_{3h} symmetry (Figure 2a). In case of P- and As-containing molecules, pyramidal structures with C_{3v} symmetry are obtained (Figure 2b). The pyramidality of P and As centers with coordination number 3 is well-known and has been found before for inorganic benzenes,[20f] dimeric $[XMYH]_2$[21] (X = F−I, M = Al−In), and monomeric X_2MYH_2[22] species. Note, that in $[HM(P,As)H]_3$ trimers all hydrogen atoms are cis-oriented (located at one side of the M_3Y_3 core). A similar situation was observed earlier for the $[XMYH]_2$ dimers, where “cis” isomers with C_{2v} symmetry were predicted to be 5−20 kJ mol−^{1} more stable compared to “trans” isomers with C_{2h} symmetry.[21] A case study of the $[HAlPH]_3$ conformers (with different orientation of the lone pairs) performed in the present work revealed the same trend. A structure with one inverted lone pair at phosphorus lies 16 kJ mol^{-1} higher in energy; a structure with all three lone pairs inverted (with trans orientation of hydrogens) is 55 kJ mol^{-1} higher in energy compared to the structure with cis-oriented hydrogens. Therefore, we expect that the cis conformation of inorganic benzenes shown of the Figure 2b is the most stable. The same is expected to hold for the mixed rings as well.

Formally, the composition $[BAlGaNPAs]H_6$ may be achieved by six different combinations of individual homoatomic $[HMYH]_3$ cycles. In Figure 3 relative energies of the isomers **I**−**VI** are compared with relative energies of the mixtures of homoatomic cyclic compounds having the same composition.

The lowest in energy is a $(1/3)[HBNH]_3 + (1/3)[HAlPH]_3 + (1/3)[HGaAsH]_3$ mixture, closely followed by $(1/3)[HBNH]_3 + (1/3)[HAlAsH]_3 + (1/3)[HGaPH]_3$. These results are in line the with higher stability of the B−N moiety in the cycle. Note that even the most stable mixed isomer **I** is higher in energy compared to $(1/3)[HBNH]_3 + (1/3)[HAlPH]_3 + (1/3)[HGaAsH]_3$.

One of the most used synthetic paths of production of group 13−15 rings and clusters is the elimination reaction sequence starting from the donor−acceptor complexes and ending at the group 13−15 binary material MY:

$$R_3MYR'H_2 \xrightarrow{-HR} (1/m)[R_2MYR'H]_m \xrightarrow{-HR} (1/n)[RMYR']_n \xrightarrow{-RR'} MY$$

The oligomerization degree m, n depends on the steric bulk of the substituent R,R′. With very bulky substituents the synthesis of trimeric compounds $[RMYR']_3$ is possible.[25]

Let us consider the possibility of formation of mixed rings and predict the most promising precursors for their synthesis.

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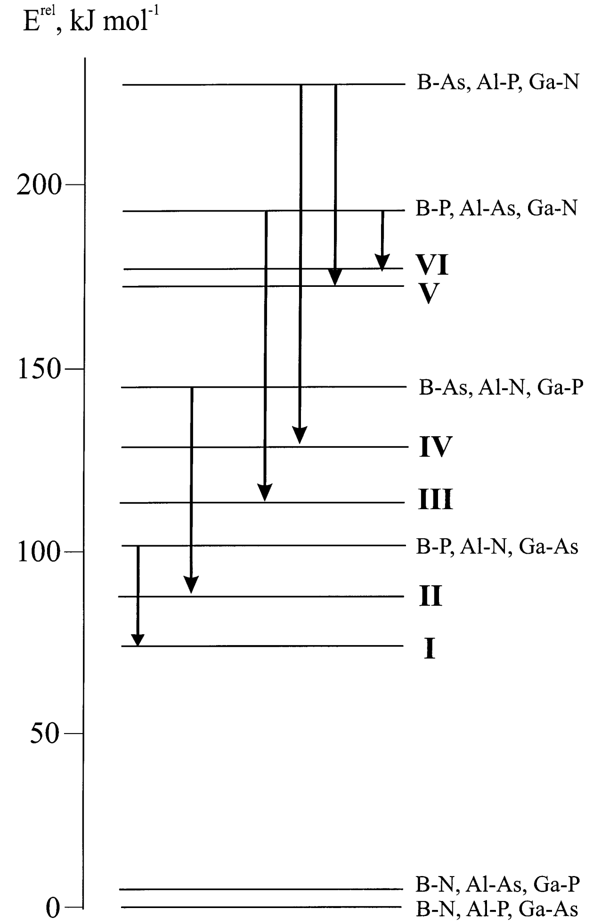

Figure 3. Relative energies of the $[BAlGaNPAs]H_6$ isomers and mixtures of $(1/3)[HMYH]_3 + (1/3)[HM'Y'H]_3 + (1/3)[HM''Y''H]_3$ trimers at B3LYP/TZVP. The most favorable precursor system for each isomer is indicated by arrows.

As an example, we will consider formation of the most stable isomer **I**. It has a $\overline{\text{B}-\text{N}-\text{Al}-\text{As}-\text{Ga}-\text{P}}$ bonding pattern, which may be divided into two groups of bonds. One combination includes B−N, Al−As, and Ga−P bonds, the second one Al−N, Ga−As, and B−P bonds. Isomer **I** lies 67 kJ mol^{-1} *higher* compared to $(1/3)[HBNH]_3 + (1/3)[HAlAsH]_3 + (1/3)[HGaPH]_3$, and therefore its synthesis by mixing of the B−N, Al−As, and Ga−P bonded precursors is thermodynamically prohibited. On the other hand, **I** lies 28.6 kJ mol^{-1} *lower* compared to the energy of $(1/3)[HAlNH]_3 + (1/3)[HGaAsH]_3 + (1/3)[HBPH]_3$, and therefore its formation from Al−N, Ga−As, B−P bonded precursors is thermodynamically favorable.

Of course, simple mixing of the corresponding homoatomic rings $[RMYH]_3$ (which, with exception of borazine, are not experimentally known so far for R = H)[25] will not afford the desired $R_3[BAlGaNPAs]H_3$ isomer. However, suitable elimination reactions starting from R_3AlNH_3, R_3GaAsH_3, and R_3BPH_3 are predicted to yield the desired mixed heterocycle **I**, while elimination from R_3BNH_3, R_3AlAsH_3, and R_3GaPH_3 are expected to be ineffective. This follows from the comparison of energetics of two possible elimination reactions (Table 4). For the precursor system 1, formation of the mixed compound is always more favorable compared to that of individual trimers. In contrast, formation of a mixed compound from the precursor system 2 is less favorable compared to that of individual trimers.

The monomeric R_2MYH_2 compounds may also be suitable precursors for the synthesis of mixed rings. Experimentally known $R_2MYR'_2$ monomers usually have bulky protecting groups R,R′ and additional donor stabilization to preclude dimerization reactions.[26] Experimental attempts to synthesize isomers with R = H need to involve the donor−acceptor stabilization of the intermediates and products. In fact, donor−acceptor stabilized monomeric $(Me_3N)H_2MPH_2(W(CO)_5)$ compounds (M = Al, Ga) have been recently synthesized by Ulf [23] by H_2 elimination from $W(CO)_5PH_3$ and MH_3NMe_3. As indicated by recent studies, $(Me_3N)H_2MPH_2(W(CO)_5)$ is serving as a starting material toward further H_2 elimination with formation of donor−acceptor stabilized dimeric and trimeric rings.[24] Since donor−acceptor bonding prevents further association processes (such as dimerization), appropriate mixtures of donor−acceptor stabilized H_2MYH_2 compounds may yield the desired $[BAlGaNPAs]H_6$ isomer (donor−acceptor stabilized). The bonding pattern of the most promising precursor systems are indicated in Table 1, and the energies of the H_2 elimination from the corresponding mixture of H_3MYH_3 donor−acceptor species are given in Table 4.

Since even high lying isomers **V** and **VI** are *lower* in energy compared to both $(1/3)[HBPH]_3 + (1/3)[HAlAsH]_3 + (1/3)[HGaNH]_3$ and $(1/3)[HBAsH]_3 + (1/3)[HAlPH]_3 + (1/3)[HGaNH]_3$, for each isomer **I**−**VI** there exists a precursor system from which the formation of a given isomer is thermodynamically more favorable than formation of a mixture of individual rings. Due to the high stability of the B−N bond in $[HBNH]_3$, precursors containing such bonding are predicted to be ineffective reagents for the synthesis of all isomers and their use should be avoided.

As was shown in our previous theoretical studies devoted to GaN CVD,[27] from the thermodynamic point of view a hydrogen atom is a satisfactory model for the methyl group. Therefore the results obtained in the present report for the hydrogen-substituted species are expected to be a qualitatively correct description of the thermodynamic behavior of the more complex systems $R_3[BAlGaNPAs]H_3$ and $[RMYH]_3$ with organic substituents R.

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Table 4. Standard Enthalpies of the Elimination Reactions (kJ mol^{-1}) of the Donor−Acceptor Complexes H_3MYH_3 with Formation of the Mixed Isomers $[BAlGaNPAs]H_6$ Compared to the Elimination Reaction with Formation of the Mixture of Individual Trimers $[HMYH]_3$, $[HM'Y'H]_3$, and $[HM''Y''H]_3$ at B3LYP/TZVP[a]

	precursor system 1			precursor system 2		
isomer	MY, M′Y′, M″Y″	$\Delta H^0{}_{(298)}{}^{elim}$	$\Delta H^0{}_{(298)}{}^{trimers}$	MY, M′Y′, M″Y″	$\Delta H^0{}_{(298)}{}^{elim}$	$\Delta H^0{}_{(298)}{}^{trimers}$
I	AlN, GaAs, BP	−113.6	−87.5	BN, AlAs, GaP	−141.4	−205.3
II	BAs, AlN, GaP	−116.1	−60.9	BN, AlP, GaAs	−126.8	−209.4
III	BP, GaN, AlAs	−93.9	−16.2	BN, GaAs, AlP	−100.3	−209.4
IV	BAs, AlP, GaN	−91.8	6.3	BN, GaP, AlAs	−87.0	−205.3
V	BAs, AlP, GaN	−50.3	6.3	BP, AlN, GaAs	−17.7	−87.5
VI	BP, AlAs, GaN	−33.5	−16.2	BAs, AlN, GaP	−29.4	−60.9

[α] $\Delta H^0{}_{(298)}{}^{elim}$ is the standard enthalpy of the reaction: $H_3MYH_3 + H_3M'Y'_3 + H_3M''Y''_3 = [BAlGaNPAs]H_6 + 6H_2$. $\Delta H^0{}_{(298)}{}^{trimers}$ is the standard enthalpy of the reaction: $H_3MYH_3 + H_3M'Y'_3 + H_3M''Y''_3 = (1/3)[HMYH]_3 + (1/3)\ [HM'Y'H]_3 + (1/3)\ [HM''Y''H]_3 + 6H_2$.

Table 5. Geometric Parameters of Hexamer $[HMYH]_6$ Compounds Predicted at B3LYP/TZVP and Energetic Characteristics of Their Dissociation into Trimers[a]

MY	R(M−Y)	R(H−M)	R(Y−H)	−MYM	−YMY	$\Delta H^0{}_{(298)}$	$\Delta S^0{}_{(298)}$	$\Delta G^0{}_{(298)}$
CC	1.558	1.090	1.090	120.0	120.0	−603.0	222.6	−669.4
	(1.565)			(90.0)	(90.0)			
BN	1.559	1.198	1.010	123.3	115.3	−293.1	249.7	−367.5
	(1.643)			(86.2)	(93.7)			
BP	2.007	1.192	1.419	123.4	116.6	30.3	270.9	−50.4
	(2.017)			(90.2)	(89.7)			
BAs	2.116	1.190	1.513	123.7	116.3	37.1	253.6	−38.5
	(2.124)			(90.0)	(89.9)			
AlN	1.911	1.584	1.016	126.2	113.7	463.3	279.2	380.1
	(1.980)			(90.2)	(89.5)			
AlP	2.423	1.581	1.415	127.9	111.4	282.5	243.1	210.0
	(2.446)			(88.7)	(90.7)			
AlAs	2.521	1.581	1.507	128.3	111.2	211.9	260.7	134.1
	(2.538)			(89.4)	(90.0)			
GaN	1.968	1.565	1.015	126.7	113.3	324.1	268.8	243.9
	(2.054)			(91.5)	(88.1)			
GaP	2.431	1.565	1.418	127.6	112.3	155.4	239.5	83.9
	(2.453)			(90.8)	(88.7)			
GaAs	2.530	1.566	1.512	128.1	111.9	99.5	258.3	22.5
	(2.539)			(91.1)	(88.3)			

[a] Bond distances are in angstroms, bond angles are in degrees, standard dissociation enthalpies $\Delta H^0{}_{(298)}$and Gibbs energies $\Delta G^0{}_{(298)}$ are in kJ mol^{-1}, standard entropies $\Delta S^0{}_{(298)}$ are in J mol^{-1} K^{-1}. [a] Values in the first row are for the six-membered ring, values in the second row (in parentheses) are for the four-membered ring. Thermodynamic parameters are given for the reaction $[HMYH]_6 = 2[HMYH]_3$.

B. Dimerization Processes. Since all M and Y atoms in the $[HMYH]_3$ and $[BAlGaNPAs]H_6$ rings are unsaturated (low coordination number 3), their dimerization processes should be considered. First, we will consider the dimerization enthalpies of the $[HMYH]_3$ rings yielding hexanuclear clusters $[HMYH]_6$. The general structure of these hexamer compounds with D_{3d} symmetry is given in Figure 2c. Optimized structural parameters are given in Table 5 together with calculated dimerization enthalpies.

The MY bonds are significantly elongated upon dimerization, as follows from the comparison of MY bond lengths given in Tables 3 and 5. The elongation is most pronounced for the C−C bond (elongating by 0.17 Å, 12% increase), followed by the B−Y bonds (6−9% increase), while the Al−Y and Ga−Y bonds are lengthened by 4−6% compared to the trimers. The MY bonds in the hexamers are inequivalent: the bonds in the six-membered cycle are generally shorter compared to bonds in four-membered cycle. However, the difference between two bond lengths is not large.

Note that the dimerization of $[HBNH]_3$ is strongly *endothermic* (by 293 kJ mol^{-1}), in contrast to all other group 13−15 species. Thus, borazine follows the pattern of benzene, for which the dimerization yielding $C_{12}H_{12}$ prismane is predicted to be even more endothermic (by 603 kJ mol^{-1}). Therefore, the aromaticity in borazine strongly deviate its behaivior from 13 to 15 heavier analogues, for which dimerization energies are *exothermic*. Recently Jemmis and co-workers[28] examined reactivity as a new characteristic property of aromaticity and concluded that the stability of the σ-complex obtained by protonation or methylation is a good indicator of aromaticity. They concluded that the aromaticity of borazine is about half the aromaticity of benzene, which is in agreement with earlier data for resonance energies (46.4 kJ mol^{-1} for borazine and 92.5 kJ mol^{-1} for benzene).[20d] Lower aromaticity of borazine is also in line with NICS criterion of Schleyer and co-workers[20c] (NICS values are −10.7 and −3.2 for benzene and borazene, respectively). If we consider dimerization enthalpies of $[HMYH]_3$ as criterion of their aromaticity, then we conclude that among the 10 considered $[HMYH]_3$ species only borazine and benzene are aromatic and that the degree of aromaticity of borazine is about half of that in benzene, in agreement with the results of Gordon[20d] and Jemmis.[28] Note, that in all earlier theoretical studies $[HBPH]_3$ was considered to be moderately aromatic (NICS value for $[HBPH]_3$ is −8.7).[20c] This in part may be attributed to the fact that a D_{3h}

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Table 6. Bonding Pattern[a] for Different Isomers, Calculated Relative Energies E^{Rel} at B3LYP/TZVP and Estimated on the Basis of MY Bond Energies Relative Energies $E^{\text{rel}}_{\text{estim}}$; Dimerization Energies[b] E^{dimer}, kJ mol^{-1}

	no. of MY bonds in isomer											
isomer	BN	AlN	GaN	BP	AlP	GaP	BAs	AlAs	GaA s	E^{rel} TZVP	E^{rel} estim	E^{dimer}
monomers												
I	1	1	0	1	0	1	0	1	1	0	0.0	
II	1	1	0	0	1	1	1	0	1	13.2	18.4	
III	1	0	1	1	1	0	0	1	1	39.3	42.5	
IV	1	0	1	0	1	1	1	1	0	55.1	63.9	
V	0	1	1	1	1	0	1	0	1	99.4	111.9	
VI	0	1	1	1	0	1	1	1	0	102.8	140.8	
dimers												
I + **I** via BN	2 + 2	2	0	2	0	2 + 2	0	2 + 2	2	0	0.0	−87.6
I + **I** rotated	2 + 1	2 + 1	0	2 + 1	0	2 + 1	0	2 + 1	2 + 1	14.2	3.7	−73.4
I + **I** via AlN	2	2 + 2	0	2	0	2 + 2	0 + 2	2	2	62.4	27.9	−25.2
I + **I** via BP	2	2	0 + 2	2 + 2	0	2	0	2 + 2	2	117.1	69.1	29.5
I + **I** (C_i)	2	2	0 + 2	2	0 + 2	2	0 + 2	2	2	149.4	84.0	61.8
II + **II** (C_i)	2	2	0 + 2	0 + 2	2	2	2	0 + 2	2	140.5	85.5	26.6
IV + **IV** (C_i)	2	0 + 2	2	0 + 2	2	2	2	2	0 + 2	144.9	88.9	−52.9
V + **V** (C_i)	0 + 2	2	2	2	2	0 + 2	2	0 + 2	2	109.0	86.0	−177.3
VI + **VI** (C_i)	0 + 2	2	2	2	0 + 2	2	2	2	0 + 2	110.7	86.2	−182.5
III + **III** open (C_i)	2	0 + 2	2	2	2	0 + 2	0 + 0[c]	2	2	−50.8		−217.1

[a] For dimeric species, the number of bonds in six-membered ring are given before the + sign, and number of bonds between six-membered rings after the + sign. [b] E^{dimer} is the energy of the formation of the dimer from corresponding monomers. [c] Formation of the B−As bonds was expected but not occurred.

symmetric planar molecule, which is not a minimum on PES, was mostly considered.

Computed dimerization energies are overestimated due to the finite basis set employed. To estimate the magnitude of the error, BSSE correction was computed by the counterpoise method.[17] BSSE correction is maximal for $[\text{HAlNH}]_6$ and $[\text{HGaNH}]_6$ (22.8 and 21.4 kJ mol^{-1}, respectively [per mole of dimer]). For all other $[\text{HMYH}]_6$ pairs BSSE values lie in range 10.2−12.8 kJ mol^{-1} (per mole of dimer). Note that BSSE correction calculated by the counterpoise method is overestimated, and therefore the exact values of the dissociation energies are expected to lie between uncorrected and BSSE corrected values.

The dimerization energies of the B−P and B−As cycles are very low, which makes the standard Gibbs energy of hexamer formation in all B-containing systems endothermic, in contrast to Al and Ga systems. Thus, dimerization of *all* boron-containing rings is thermodynamically prohibited.

Due to the unsaturated character of the bonding, mixed $[\text{BAlGaNPAs}]\text{H}_6$ rings may also dimerize, aggregating themselves into clusters of $[\text{BAlGaNPAs}]_2\text{H}_{12}$ composition. There are several dimerization models possible for each isomer, and a variety of structures can be produced by mixing all possible isomers together. It is not possible at the present time to describe all possible dimeric combinations for all isomers. Therefore, instead of considering all isomers explicitly, we will test a bond energy model of predicting their stability. This model will be derived in section C. To test the applicability of the bond energy model, we considered two series of dimerization processes:

(a) different dimerization paths of the most stable isomer **I**; (b) "head to tail" dimerization of isomers **I**−**VI** with formation of C_i-symmetric dimers, which have the same number of MY bonds (two MY bonds of each kind; the difference is in the bonding pattern of the four- and six-membered cycles).

At first the dimerization of the most stable isomer **I** was considered. Bonding pattern and relative energies of the dimers are given in Table 6. The optimized structures are presented as Supporting Information.

We have also performed the optimization of $[\text{BAlGaNPAs}]_2\text{H}_{12}$ units, assuming only head-to-tail dimerization of isomers **I**−**VI** with formation of the C_i symmetric associates. All such dimers possess two bonds of each sort, however, the bonding pattern is different in essence of which bonds are in six-membered rings and which are in four-membered rings. The optimized structures are given as supporting information, relative energies are presented in Table 6.

Our results show that the dimerization enthalpies of the mixed rings may be both exo- and endothermic, depending on the bonding pattern. Indeed, the formation of a **II** + **II** dimer with newly added two Ga−N, two B−P, and two Al−As bonds is endothermic by 27 kJ mol^{-1}. At the same time, formation of **V** + **V** dimer with two B−N, two Al−As, and two Ga−P bond is exothermic by −177 kJ mol^{-1}. It is interesting that the dimerization of a **I**−**VI** ring is driven by the formation of the B−N bonds. The most exothermic enthalpies of dimerization are related to B−N bond formation (**V** + **V**; **VI** + **VI**; **I** + **I** via BN). This at first contradicts the result of high endothermicity of dimerization of pure borazine $[\text{HBNH}]_3$. However, the endothermicity of the latter arises from the aromatic stabilization of the trimeric ring $[\text{HBNH}]_3$. In the mixed $[\text{BAlGaNPAs}]\text{H}_6$ rings, there is no aromatic stabilization (only one B and one N center are present in each molecule), and therefore, formation of the shortest (and the strongest) B−N bond is most favorable thermodynamically.

The vibrational frequencies and IR intensities of the $[\text{BAlGaNPAs}]\text{H}_6$ mixed compounds are given as supporting information. They may facilitate the experimental identification of the compounds. The analysis of the computed vibrational frequencies reveals great similarities in the spectra

Table 7. Mean M−Y Bond Energies, kJ Mol^{-1} (per MY bond) in $[HMYH]_3$, $[HMYH]_4$, and $[HMYH]_6$ Calculated According to the Dissociation into MH and YH Fragments[a]

MY	$[HMYH]_3$ (mean)	$[HMYH]_6$ (mean)	$[HMYH]_4$ (four-membered cycle)	$[HMYH]_6$ (six-membered cycle)
CC	592.0	361.4	346.6	368.8
BN	496.5	314.7	302.5	320.8
BP	319.8	215.1	202.7	221.3
BAs	283.5	191.3	179.4	197.2
AlN	337.8	251.5	243.6	255.4
AlP	212.0	157.4	150.3	161.0
AlAs	194.1	141.6	134.5	145.1
GaN	266.3	196.0	189.2	199.3
GaP	183.1	131.0	124.0	134.6
GaAs	168.2	118.0	110.9	121.5

[a] For $[HMYH]_6$, mean bond energies are calculated separately for the four- and six-membered cycles. All values at B3LYP/TZVP.

of all $[BAlGaNPAs]H_6$ compounds. There is no "fingerprint" region for the given isomer, and a rather careful comparison of the spectra should be performed. Thus, IR methods are predicted to be of less help in the determination of the isomer structure. The same arguments are valid for the mixed dimers $[BAlGaNPAs]_2H_{12}$ as well.

C. Derivation of MY Bond Energies. Due to the high computational costs, considering more complex species in detail is not possible, but a simple model of the isomer stability may be helpful in estimating the synthetic paths. Recently Ziegler and coauthors[29] developed an additive scheme for $[MeAlO]_n$ clusters, based on the bonding environment of atoms in the cluster to estimate the cluster energy. This approach, however, cannot be applied for the group 13−15 mixed species, because they exhibit a diverse range of element−element bonds. In this situation, derivation of mean MY bond energies seems to be one of the simplest ways to predict relative stabilities of the complex cluster species. In a work by Yang et al.,[13] it was shown that the bond energies in four-membered cycles of group 13−15 elements $[H_2(M,M')(Y,Y')H_2]_2$ are transferable. In the present report we are testing the transferability of MY energies in trimer and hexamer compounds.

First we derive mean bond energies in $[HMYH]_3$ rings. This was done by considering a reaction of complete destruction of all six MY bonds with formation of singlet HM and triplet YH species:

$$[HMYH]_3 = 3HM + 3YH$$

The alternative reaction of dissociation of the trimers into monomers with three MY bonds breaking ($[HMYH]_3 = 3HMYH$) proved to be inadequate due to the fact of remarkable stability of linear HBNH (the only linear HMYH molecule), which leads to an underestimation of the B−N energy.

The obtained values of the MY bond energies in $[HMYH]_3$ are given in Table 7. Using these MY bond energies, a good qualitative agreement with the explicitly calculated values (correct order of relative stability of isomers **I**−**VI**) is produced. However, as can be seen from Table 6, the relative energies may be wrong by as much as 40 kJ mol^{-1}.

By analogy, the mean MY energy in hexamer $[HMYH]_6$ cluster compounds was calculated according to complete dissociation with 18 MY bonds breaking:

$$[HMYH]_6 = 6HM + 6YH$$

The obtained values are given in Table 7. Note that the mean M−Y bond energy in the hexamers is much lower compared to that in trimers, reflecting the longer MY distances. There are two type of MY bonds in $[HMYH]_6$: within six-membered rings and between these rings (in four-membered rings). Because of this, the derived mean MY bond energies in $[HMYH]_6$ cannot be used to estimate the relative energies of mixed dimers.

To show this, we calculated several "head to tail" C_i symmetric $[BAlGaNPAs]_2H_{12}$ dimers which are isobonding (having the two MY bonds of each kind, see Table 6 for detail of bond counting). If the values of mean energies of the hexamers were used, all these isomers would have the same relative energy. However, the computed B3LYP relative energies of these "isobonding" compounds are not equivalent, reflecting the inequality of the MY bonds in four- and six-membered rings. Therefore, separate values for the MY bond energy in six- and four-membered rings are needed.

The separation cannot be done simply by taking into account the dissociation of the hexamers into two trimers. This follows from the endothermicity of the dimerization of borazine, while dimerization of the monomer **I** via B−N bonding is the most favorable process which is *exothermic*. Therefore, we decided to estimate the energy of the MY bond in the four-membered ring by considering the dissociation of the $[HMYH]_4$ cubanes. All T_d symmetric $[HMYH]_4$ cubanes (Figure 2d) have been optimized at B3LYP/TZVP. The optimized structural parameters are given in Table 2S. All MY bonds in cubane are in four-membered rings, and all atoms have coordination number 4. Therefore, we expect that the mean MY bond energy, obtained from the equation

$$[HMYH]_4 = 4HM + 4YH$$

may be taken as the MY bond energy in the four-membered ring of the hexamer $[HMYH]_6$. Predicted MY distances in the $[HMYH]_4$ tetramers are close to MY distances in the four-membered rings of $[HMYH]_6$ hexamers (Table 8). For the P,As-containing species the difference between bond lengths is about 0.01 Å, for nitrogen containing species the difference is more pronounced: about 0.05 Å. The MY bond energies in the six-membered ring are now defined by using the total dissociation energy of $[HMYH]_6$ and the corresponding bond energies in the four-membered ring. The results obtained are given in Table 7.

Now the predicted MY bond energies will be used to estimate relative energies of different isomers. The results obtained are presented in the bottom part of the Table 6. The estimated values correctly predict the order of the three lowest lying isomers, and they also correctly give higher

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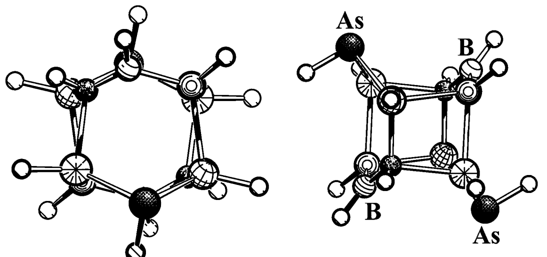
Table 8. Comparison of the M−Y Bond Distances for Investigated Compounds[a]

compound	CC	BN	BP	BAs	AlN	AlP	AlAs	GaN	GaP	GaAs
[HMYH]	1.198	1.235	1.697	1.799	1.637	2.152	2.242	1.705	2.149	2.245
$[HMYH]_3$	1.392	1.431	1.856	1.989	1.802	2.317	2.423	1.849	2.323	2.428
$[HMYH]_4$	(1.570)	(1.595)	(2.028)	(2.138)	(1.940)	(2.438)	(2.535)	(2.004)	(2.449)	(2.542)
$[HMYH]_6$	1.558, (1.565)	1.559, (1.643)	2.007, (2.017)	2.116, (2.124)	1.911, (1.980)	2.423, (2.446)	2.521, (2.538)	1.968, (2.054)	2.431, (2.453)	2.530, (2.539)
monomers										
I		1.416	1.932		1.829		2.415		2.309	2.429
II		1.412		2.051	1.831	2.307			2.329	2.407
III		1.411	1.932			2.304	2.433	1.884		2.408
IV		1.407		2.054		2.332	2.406	1.887	2.301	
V			1.881	2.020	1.794	2.325		1.860		2.420
VI			1.888	2.009	1.798		2.425	1.855	2.319	
dimers										
I + **I** (C*i*)		1.571	2.064	(2.224)	1.935	(2.407)	2.477	(2.116)	2.370	2.429
II + **II** (C*i*)		1.567	(2.045)	2.212	1.936	2.405	(2.506)	(2.142)	2.360	2.446
IV + **IV** (C*i*)		1.574	(2.058)	2.204	(1.980)	2.361	2.458	2.055	2.402	(2.510)
V + **V** (C*i*)		(1.607)	2.009	2.136	1.932	2.416	(2.519)	2.050	(2.428)	2.483
VI + **VI** (C*i*)		(1.608)	2.014	2.129	1.941	(2.423)	2.502	2.043	2.410	(2.510)
I + **I** via BN		1.575, (1.623)	2.043		1.939	(2.416)	2.504		2.414	2.514, (2.554)
I + **I** ‘rotated		1.581, 1.584, (1.626)	2.055, (2.030)		1.943, (1.983)		2.522, (2.546)		2.429, (2.451)	2.504, 2.512, (2.541)
I + **I** via AlN		1.570	2.059	(2.259)	1.922, (1.981)		2.421		2.429, (2.422)	2.473
I + **I** via BP		1.574	2.069, (2.033)		1.939		2.526, (2.526)	(2.135)	2.363	2.452
III + **III** (C*i*) open		1.438	1.906	(4.203)	(2.003)	2.449	2.456	2.227	(2.456)	2.437

[a] B3LYP/TZVP level of theory. [a] Values for the four-membered rings are given in parentheses.



III+**III** open (C_i)

Figure 4. Optimized structure of the **III** + **III** open dimer of C_i symmetry. B3LYP/TZVP level of theory.

energies for C_i symmetric structures but the quantitative agreement is very poor. Despite of quantitative discrepancies, however, we conclude that the bond energies listed in the Table 7 may be applied for a qualitative estimation of the relative stability of isomers. The poor quantitative agreement is in part due to the underestimation of the B−N bond energy in the four-membered ring, which follows from the comparison of calculated and estimated values for **V** + **V** and **IV** + **IV** isomers. A significant reorganization due to steric mismatch between "head to tail" dimerizing rings may be another factor limiting the applicability of the bond energy model. The importance of the latter factor is illustrated by the following example. During an optimization of the "head to tail" **III** + **III** isomer (C_i symmetry), a structure shown in Figure 4 emerged. It features nearly planar three-coordinated boron and pyramidal three-coordinated arsenic centers. Despite the fact that it lacks B−As bonding, it is the most stable isomer among all considered in the present work. This result can be rationalized in terms of weakeness of the B−As bond and high reorganization energy of the As center. Predicted inversion barriers for NH_3, PH_3 and AsH_3 are 27, 149 and 192 kJ mol^{-1}, respectively.[20a] The B−As bond energy in the four membered ring is 179 kJ mol^{-1} (Table 7), which does not compensate unfavorable distortion energies of the As and B centers. Dimerization energies of $[HBPH]_3$ and $[HBAsH]_3$ are very low (30 and 37 kJ mol^{-1}, respectively). Note significant shortening of the B−N and B−P distances, which are close to the values for the pure borazene and $[HBPH]_3$ (see Table 8). Thus, additional stabilization of B−N and B−P bonds may be also responsible for high stability of the partly unsaturated "open" structure.

The mean MY bond energies presented in Table 7 may also serve as values to estimate the possibility of bond breaking in the cycles. The least stable is the GaAs bond, with dissociation energy of 111−168 kJ mol^{-1}, followed by the Ga−P bond with a dissociation energy 124−183 kJ mol^{-1}. Thus, Ga−As and Ga−P bonds are expected to be most easily broken. This may explain the experimental observation that cyclic Ga−As containing precursors were found ineffective for the GaAs deposition,[11] in contrast to GaN and AlN precursors. The gallium loss observed upon converting the mixed dimeric cyclic compounds $[R_2GaYY'R'_2]_2$ (Y, Y′ = P, As, Sb) is another indicator of precursor's instability.[10] All mixed rings have either Ga−As or Ga−P bonds (or both). However, in contrast to rings which are solely Ga−As and Ga−P bonded, the mixed rings considered in the present work have only one Ga−As or Ga−P bond and therefore are expected to be more stable toward ring destruction.

4. Conclusions

Among the considered mixed inorganic analogues of benzene [BAlGaNPAs]H_6, heterocycles with a B−N bond are predicted to be exceptionally stable. Processes of the formation of heterocycles by H_2 elimination from the corresponding donor−acceptor complexes are favorable thermodynamically. Synthesis of the mixed rings is feasible from the thermodynamic point of view. For the each [BAlGaNPAs]H_6 isomer there is a precursor system from which formation of the mixed heterocycle is thermodynamically more favorable compared to formation of the mixture of the individual trimers. The synthesis of mixed compounds [BAlGaNPAs]H_6 and their organometallic derivatives may follow the path of the donor−acceptor stabilization of intermediates. The most promising synthetic target is the B−N−Al−As−Ga−P isomer, which may be formed from the Al−N, Ga−As, B−P bonded precursor systems.

The dimerization processes of mixed rings can be exo- and endothermic, depending on the bonding pattern. Dimerization of pure trimers is generally exothermic, with exception of aromatic borazine and benzene for which dimerization is endothermic. However, formation of B−N bonds between mixed rings is the most favorable process. 13−15 bond energies were derived for ring and cluster compounds and may serve for a qualitative prediction of relative stability of isomers of mixed 13−15 clusters [HMYH]$_n$. However, applicability of the bond energy model is limited due to steric and reorganization effects. Inorganic analogues of benzene, "true" heterocycles [BAlGaNPAs]H_6 and their dimers are not "curiosities" in the inorganic chemistry world, but they are predicted to serve as advanced single-source precursors for the formation of novel materials and group 13−15 composites. Substitution of a group 13 metal by a rare-earth metal (lanthanides and actinides) may also be possible, making a step toward stoichiometry controlled synthesis of doped group 13−15 materials.

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Supporting Information Available: Geometric parameters and dissociation energies of [HMYH] species, structural parameters of T_d symmetric [HMYH]$_4$ cubanes, structures, and Cartesian coordinates of the [BAlGaNPAs]$_2H_{12}$ isomers, predicted vibrational frequencies and IR intensities for the [BAlGaNPAs]H_6 and [BAlGaNPAs]$_2H_{12}$, the total energies of all compounds at the B3LYP/TZVP level of theory (14 pages). The material is available free of charge via the Internet at http://pubs.acs.org.

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