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Pi Bonding and Negative Hyperconjugation in Mono-, Di-, and Triaminoborane, -alane, -gallane, and -indane

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A systematic quantum chemical investigation of mono-, di-, and triaminoborane, -alane, -gallane, and -indane is carried out to determine quantitatively the effects of pi bonding and negative hyperconjugation on structures, energetics, and rotational barriers in these systems. Pi bonding plays a significant role in the aminoborane compounds, but becomes rapidly less significant in the aminoalanes, -gallanes, and -indanes. For each main-group metal X investigated, X–N rotational barriers are found to be essentially equal depending only on the number of remaining in-plane amino groups. The contribution of negative hyperconjugation to reducing rotational barriers, as assessed from natural bond orbital (NBO) delocalization energies, is independent of the pyramidalization of the out-of-plane amino group, and is also dependent only on the number of rotated groups. Optimized tris[bis(trimethylsilyl)amino]-substituted structures of boron, aluminum, gallium, and indium are found to compare quite well with available experimental structural data, and exhibit X–N torsion angles that are independent of the central metal atom.

Introduction

The study of compounds involving nitrogen and a group 13 metal are of great interest because of the potential for pi bonding via overlap of the lone electron pair on nitrogen with the empty p orbital on the metal.[1−3] Beyond their intrinsic interest, such compounds have utility for the synthesis of group 13 nitride semiconductors.[4]

One indication of pi bonding in these compounds is shortening of the X−N (X = group 13 metal) bond length compared to a typical X−N single bond (or compared to the sum of the covalent radii).[1] However, bond shortening does not necessarily have to be indicative of pi bonding; it can also be caused by ionic interactions due to differences in electronegativity.[1,2] Another indication of pi bonding is a barrier to rotation around the X−N bond.[1] However, this measure can be complicated by steric factors. It is generally necessary to use bulky substituents in order to obtain monomeric structures,[1,2,4] so measured barriers do not necessarily reflect the energetics of isolated pi bonding. Moreover, bulky substituents can also complicate matters by playing a role in bond lengthening.[1]

There is significant evidence for pi bonding in aminoboranes.[5−16] An increase in B−N bond lengths is observed upon an increasing number of amino substituents, that is, the B−N bond length in a monoaminoborane is shorter than those in a diaminoborane, which in turn are shorter than those in a triaminoborane. This may be taken as an indication of competition for the single empty p orbital on boron by the increasing number of nitrogen lone pairs, leading to a decrease in each individual pi bond strength. Substantial barriers to rotation around the B−N bond have also been determined for substituted aminoboranes, ranging from 5 to 25 kcal mol^{-1}.[5−16]

The evidence for pi bonding in aminoalanes, -gallanes, and -indanes, however, is not as strong. Changes in bond

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lengths of aminoalane and -gallane compounds are generally viewed as an indication of ionic effects rather than pi bonding,[1,2,17] insofar as no discernible trends have been clearly established when comparing X−N bond lengths for cases with an increasing number of amino substituents. If anything, the opposite trend seems to be true: there is more of a general decrease in X−N bond lengths upon increasing amino substitution.[1,2,18,19] Practical considerations have often motivated a preference for steric bulk in the monoamines over optimal pi overlap, leading to higher torsion angles and longer X−N bonds.[1,18] Though some experimental barriers to rotation have been observed in aminoalane, -gallane, and -indane compounds, it is not always clear whether that is due to pi bonding or due to other factors associated with the bulky substituents, as mentioned above. The general consensus on aminoalanes, -gallanes, and -indanes is that the major contribution to changes in bond length is an ionic resonance effect; however, there may be a small pi bonding effect with a maximum magnitude of 9−10 kcal mol^{-1}.[1,2,18−23]

In order to differentiate electronic effects from steric effects caused by the bulky substituents that have been employed experimentally, we here carry out a systematic quantum chemical study of mono-, di-, and triaminoborane, -alane, -gallane, and -indane. Not only can such a study characterize the pi bonding interactions without the interference of steric interactions, but the pi bonding can also be analyzed as a function of the group 13 metal. The importance of other interactions on the rotational coordinate, such as negative hyperconjugation, can be investigated as well.

Computational Methods

All structures were optimized at the density functional (DFT) level of theory using Becke 3 hybrid exchange (B3)[24] with Lee, Yang, and Parr correlation[25] (B3LYP). Optimizations of B**1**−B**2**, Al**1**−Al**2**, Ga**1**, and In**1** structures were also performed with Møller−Plesset second-order perturbation theory (MP2) for comparison.[26] Both methods employed the 6-311+G(2df,p) basis set.[27−30] Modeling of the larger, many-electron gallane and indane metals was facilitated by the use of an effective core potential (ECP). When compared to all electron calculations with the 6-311+G(2df,p) basis set, the compact effective core potential (CEP) of Stevens, Basch, and Krauss[31−33] was found to be superior to the Los Alamos ECP, LanL2DZ,[34−36] and this basis was therefore used for modeling of the more highly substituted aminogallane and -indane systems. CEP1 implies use of the CEP ECP basis set on Ga or In and the 6-311+G(2df,p) basis set on H and N; CEP2 implies use of the CEP ECP basis set on In and the 6-31G(d) basis set[37,38] on H and N. All optimized molecular geometries were characterized by frequency calculations and subjected to natural bond orbital (NBO) analysis[39−45] at the B3LYP level. The NBO calculations enable quantification of hyperconjugative interactions between the nitrogen lone pair and unfilled X−H or X−N antibonding orbitals ($n \rightarrow \sigma^*$) from second-order perturbation theory.[46]

Single-point energy calculations using coupled cluster theory with single, double, and perturbative triple excitations (CCSD(T))[47−51] were performed on the B3LYP and MP2 optimized structures of B**1**−B**2**, Al**1**−Al**2**, Ga**1**, and In**1**. These calculations employed the 6-311+G(2df,p) basis set for all species except those involving In, which instead used the CEP1 basis set (as defined above). Larger tris[bis(trimethylsilyl)amino]-substituted systems were also optimized using B3LYP. The basis set employed for these structures was 6-31G(d) on B and N; CEP-31G(d) on Al and Si; CEP-31G on Ga and In; MIDI![52] on C; and STO-3G[53,54] on H. All calculations were performed using Gaussian98, revision A.9.[55]

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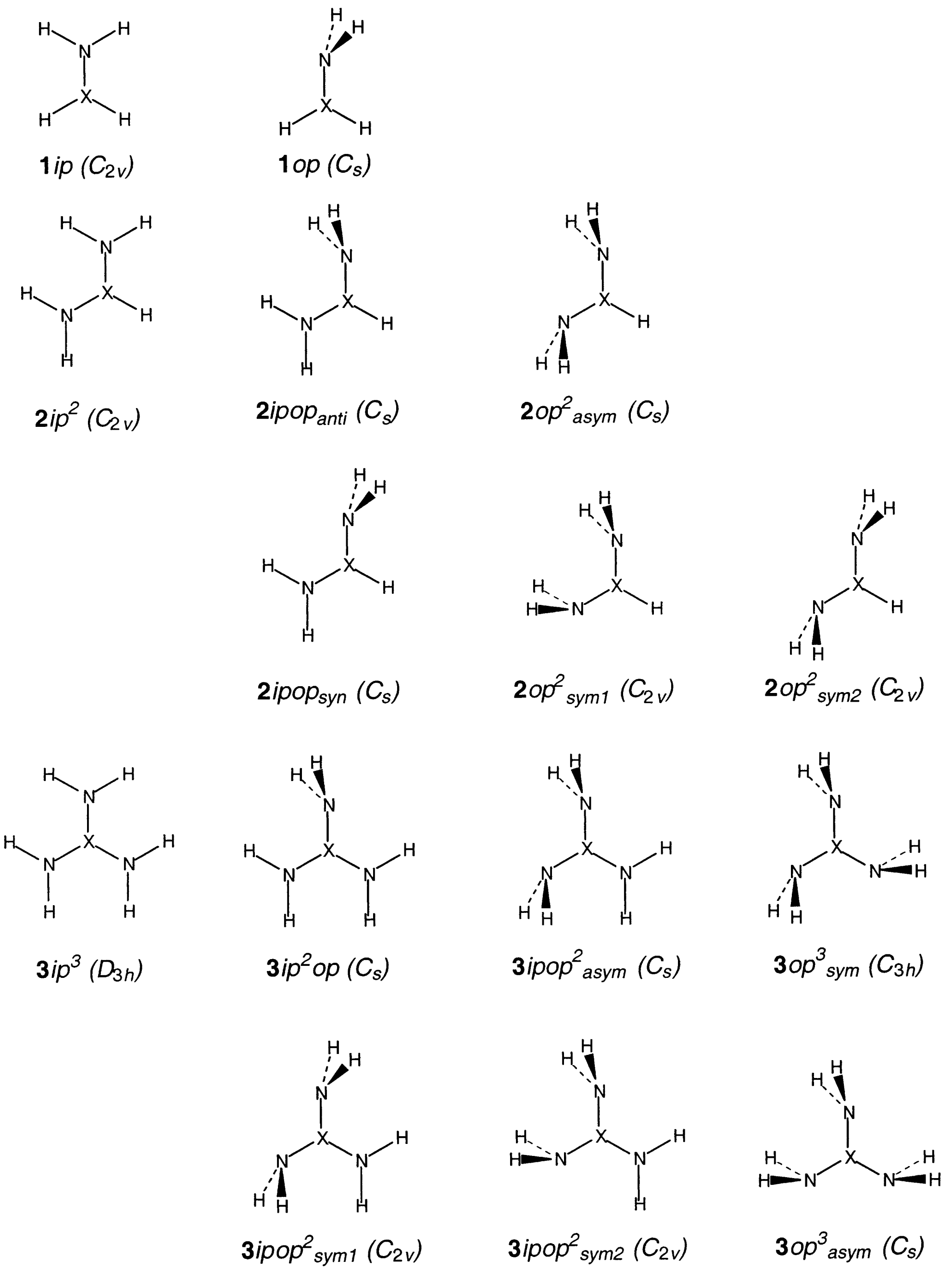

Figure 1. Nomenclature for conformers. Not all structures are stationary for all group 13 atoms. In addition, subtleties associated with pyramidalization of in-plane amino groups are encountered in several instances, as detailed in the text.

Results and Discussion

Nomenclature. The structures of the conformers investigated in this study can be found in Figure 1, labeled with their symmetry and named according to the following convention. The first character indicates the group 13 metal: B, Al, Ga, or In. The numbers **1**, **2**, and **3** indicate the number of amino substituents attached to the metal. The ip^m and op^n labels indicate whether the amino group(s) are in-plane or out-of-plane with respect to the remaining X−N or X−H bonds, and the superscripts m, $n = 2-3$ indicate the number of each type (for simplicity, a superscript "1" is taken to be the default if no other value is present). Subscripts indicate the orientations of the lone pairs on pyramidalized out-of-plane amino groups when multiple stereoisomers are possible. Structures in which the amino group is *op* but constrained by symmetry *not* to pyramidalize are indicated by the label *op-pl*; these structures are not presented in detail, but their pertinent energetics are discussed when necessary.

B1-B3. The unique B−N bond lengths for structures B**1**−B**3** are reported in Table 1, and the relative energetics for these structures are listed in Table 2. Also reported in Table 2 are the NBO delocalization energies associated with $n_N \rightarrow \sigma^*$ negative hyperconjugation; the listed values represent the sums of the delocalization energies associated with all possible combinations of in-plane lone pairs (i.e., those from *op* amino groups) and acceptor σ^* orbitals. The latter orbitals

Table 1. B−N Bond Lengths for Structures B**1**−B**3** Optimized at Various Levels of Theory

structure	bond lengths (Å)^a in-plane 1	in-plane 2	out-of-plane 1	out-of-plane 2	out-of-plane 3
B3LYP/6-311+G(2df,p) Level					
B**1***ip*	1.388				
B**1***op*	1.467				
B**2***ip*^{2}	1.413				
B**2***ipop*$_{anti}$	1.397		1.474		
B**2***ipop*$_{syn}$	1.391		1.477		
B**2***op*$^2_{asym}$			1.466	1.476	
B**2***op*$^2_{sym1}$			1.475		
B**2***op*$^2_{sym2}$			1.468		
B**3***ip*^{3}	1.430				
B**3***ip*^{2}*op*	1.416	1.423	1.483		
B**3***ipop*$^2_{asym}$	1.401		1.483	1.488	
B**3***ipop*$^2_{sym1}$	1.409		1.483		
B**3***ipop*$^2_{sym2}$	1.396		1.488		
B**3***op*$^3_{sym}$			1.481		
B**3***op*$^3_{asym}$			1.473	1.481	1.495
MP2/6-311+G(2df,p) Level					
B**1***ip*	1.392				
B**1***op*	1.472				
B**2***ip*^{2}	1.414				
B**2***ipop*$_{anti}$	1.400		1.477		
B**2***ipop*$_{syn}$	1.393		1.480		
B**2***op*$^2_{asym}$			1.469	1.480	
B**2***op*$^2_{sym1}$			1.479		
B**2***op*$^2_{sym2}$			1.471		

[a] Only one length is reported when two or more bonds are identical by symmetry.

Table 2. Relative and NBO Delocalization Energies (kcal mol^{-1}) for B**1**−B**3** Stationary Points at Various Levels of Theory

structure	no. of ν_{imag}	relative energy^a B3LYP	MP2	CCSD(T)// B3LYP	CCSD(T)// MP2	E_{deloc}
B**1***ip*	0	0.0	0.0	0.0	0.0	0.0
B**1***op*	1	32.4	32.2	32.1	32.2	12.6
B**2***ip*^{2}	0	0.0	0.0	0.0	0.0	0.0
B**2***ipop*$_{anti}$	1	17.1	17.0	16.6	16.6	15.2
B**2***ipop*$_{syn}$	1	14.5	14.4	13.9	13.9	16.0
B**2***op*$^2_{asym}$	2	44.9	44.7	44.1	44.1	26.9
B**2***op*$^2_{sym1}$	2	46.6	46.5	45.9	45.9	28.7
B**2***op*$^2_{sym2}$	2	46.1	46.2	45.6	45.5	28.7
B**3***ip*^{3}	0	0.0				0.0
B**3***ip*^{2}*op*	1	8.3				16.7
B**3***ipop*$^2_{asym}$	2	23.9				31.5
B**3***ipop*$^2_{sym1}$	2	27.7				31.7
B**3***ipop*$^2_{sym2}$	2	22.6				34.8
B**3***op*$^3_{sym}$	3	51.2				42.0
B**3***op*$^3_{asym}$	3	54.6				45.8

[a] All energies computed with 6-311+G(2df,p) basis set and reported relative to isomeric local minimum.

may be of either the XH or XN variety: the magnitudes of the delocalization energies associated with these two types of acceptor orbitals were typically quite similar in all systems.

The B−N bond lengths for the B**1***ip* structure, 1.388 Å at B3LYP and 1.392 Å at MP2, are in excellent agreement with the experimental value of 1.391 Å.[12] As reported in previous studies,[13−16] the planar B**1***ip* structure has a much shorter B−N bond length than that of B**1***op*, and this is attributed to pi bonding.[1,2,5,8,10,13−15] When rotated out of plane, the B−N bond lengthens by 0.079 Å, a change very similar to those found in other computational studies (0.082,[13] 0.084,[14] 0.076,[15] and 0.079 Å[16]). Another indication of pi bonding is the barrier to rotation about the B−N bond, i.e., the energy difference between the B**1***ip* and B**1***op* structures. This energy difference is strikingly similar for all four levels of theory, ranging from 32.1 kcal mol^{-1} at CCSD(T)//B3LYP to 32.4 kcal mol^{-1} at B3LYP. These values are in good agreement with values previously reported: 33.3,[56] 29.4,[57] 33.8,[58] 34.2,[59] 33.0,[60] 32.1,[14] 32.4,[15] 33.5,[61] and 29.0[16] kcal mol^{-1}. Experimental free energy barriers for the rotation around substituted monoaminoboranes range from 17 to 24 kcal mol^{-1};[6,8,10,62−64] these values are substantially lower than the value of 29.8 kcal mol^{-1} obtained from B3LYP (after inclusion of thermal contributions) for B**1**. This difference likely derives from both electrostatic and steric considerations associated with hydrogenic substitution in the theoretical model compared to alkyl substitution in the experimental cases. With respect to electrostatics, the hydrogens attached to the nitrogen and boron atoms have opposite partial atomic charges ($\delta+$ when attached to nitrogen; $\delta-$ when attached to boron); the favorable interaction between these atoms when the amino group is in-plane increases the computed barrier to rotation. In addition, the bulkier substituents on the experimental monoaminoboranes sterically destabilize the planar conformer and thereby contribute to a lower barrier to rotation.

The preferred minimum energy conformation upon addition of the second amino group to boron is again the planar structure, B**2***ip*^{2}. The B−N bond lengths in the diamino B**2***ip*^{2} structure of 1.413 Å (B3LYP) or 1.414 Å (MP2) agree quite well with the experimental B−N bond length of 1.418 Å.[11] The B**2***ip*^{2} bond lengths are 0.025 Å longer than those in the monoamino B**1***ip* structure. This bond lengthening has been ascribed to competition of the two lone electron pairs on the nitrogens for overlap with the lone empty p orbital on boron.[1,12] Weaker pi bonding is manifest in the predicted rotational barriers. Addition of the second amino substituent decreases the barrier to rotation of the first amino group to 16.6 (B**2***ipop*$_{anti}$) or 13.9 kcal mol^{-1} (B**2***ipop*$_{syn}$), depending on the orientation of the lone electron pair on the *op* pyramidalized nitrogen in the transition-state (TS) structure. Examination of the NBO delocalization energies reveals that they are quantitatively about the same for both the B**2***ipop*$_{anti}$ and B**2***ipop*$_{syn}$ structures. Thus, the difference in energy between the two TS structures is probably partly steric and partly electrostatic, with the hydrogen atoms of the rotated, pyramidalized amino group preferring to orient toward the small, partially negatively charged hydrogen atom bound to boron.

After the first amino group is rotated out-of-plane, the B−N bond length of the remaining *ip* amino group decreases

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by up to 0.022 Å, suggesting an increased pi interaction, and the B−N bond length of the *op* amino group increases by up to 0.066 Å, consistent with a decreased pi interaction. This decrease in pi bond strength has also been observed in experimental rotation energies of substituted diaminoboranes,[8−10,65] though a steric component can also contribute to the decreased rotational barriers when bulky substituents are added to one of the amino groups.[10] Rotation of the *second* amino group in diaminoborane can lead to three different conformers: B**2**op^{2}_{sym1} in which the amino lone pairs are both oriented toward the B−H bond, B**2**op^{2}_{sym2} in which the amino lone pairs are both oriented antiplanar to the B−H bond, and B**2**op^{2}_{asym} in which one lone pair is oriented toward the B−H bond and the other is oriented toward the other amino group. As expected, when the second amino group is rotated out-of-plane, its B−N bond lengthens due to the decrease in pi bonding by up to 0.087 Å, a distance similar to the lengthening of the single B−N bond in the B**1***op* structure. The energy required to rotate the second amino group out-of-plane is approximately equivalent for each of the three conformations (∼30 kcal mol^{-1}), which is about the same amount of energy required to rotate the amino group in the B**1** structure. Thus, consistent with the failure of the NBO delocalization energies to show any dependence on the nature of the acceptor orbital, BN vs BH, the total energy for rotating the two amino groups out of plane in the diamino system may be computed by summing the energy associated with the unique initial rotational energy and the value computed in the monosubstituted system for the remaining amino group.

The B**3** structures follow the trends established in the B**2** system. The planar structure, B**3**ip^{3}, is again the lowest energy structure, and the B−N bonds are longer still than in the B**2**ip^{2} structure at 1.430 Å, which is again due to competition of the now *three* nitrogen lone pairs for the one empty boron p orbital. It has been reported that pi bonding is limited to only two of the B−N bonds in substituted triaminoboranes because these structures typically show two short B−N bonds and one long B−N bond.[1,66] This seems not to be the case with triaminoborane, in that the C_{3v} planar structure is indeed the (global) minimum on the potential energy surface as judged from analytic frequency calculations. However, it is certainly the case that the pi bonding between B and any one amino group is indeed much weaker in the B**3**ip^{3} system than in the former two, since the barrier to rotation of the first amino group is reduced to 8.3 kcal mol^{-1}. In this B**3**$ip^{2}op$ structure, the *ip* B−N bonds decrease while the *op* one increases, and when the second amino group is rotated out-of-plane in the B**3**$ipop^{2}$ structures, the remaining *ip* B−N bond decreases further still. As with the B**2** structures, the NBO delocalization energies do not reveal any dependence on the orientation of the *op* amino groups, and the rotational barriers for the second amino group, to generate B**3**$ipop^{2}$ structures, and the last amino group, to generate B**3**op^{3} structures, are quantitatively very close to the analogous barriers computed in B**2** and B**1**, respectively. That is, the total barrier may be computed in an additive fashion without reference to the nature of non-pi-conjugated groups. Consistent with this additivity observation is the prediction that the delocalization energy associated with negative hyperconjugation is also additive. It is effectively 13−14 kcal mol^{-1} per rotated amino group in any structure.

Table 3. Al−N Bond Lengths for Structures Al**1**−Al**3** Optimized at Various Levels of Theory

	bond lengths (Å)[a]				
	in-plane		out-of-plane		
structure	1	2	1	2	3
B3LYP/6-311+G(2df,p) Level					
Al**1***ip*	1.773				
Al**1***op*	1.794				
Al**2**ip^{2}	1.776				
Al**2**$ipop^{b}$	1.772		1.791		
Al**2**$op^{2\ b}$			1.800		
Al**3**$ip^{3\ c}$	1.778				
Al**3**$ip^{2}op$	1.776		1.787		
Al**3**$ipop^{2\ b}$	1.770		1.799		
Al**3**op^{3}_{sym}			1.809		
Al**3**op^{3}_{asym}			1.802	1.804	1.811
MP2/6-311+G(2df,p) Level					
Al**1***ip*	1.776				
Al**1***op*	1.798				
Al**2**ip^{2}	1.778				
Al**2**$ipop^{b}$	1.774		1.794		
Al**2**$op^{2\ b}$			1.803		

[a] Only one length is reported when two or more bonds are identical by symmetry. [b] Out-of-plane amino group(s) is/are approximately planar so isomers related by inversion do not exist. [c] Structure has one very small imaginary frequency, but a C_1 minimum is computed to be only 0.02 kcal mol^{-1} lower in energy, and when zero-point vibrational energy is included, the C_1 structure is higher in energy than the D_{3h} one, suggesting that this species is pseudo-planar.

Table 4. Relative and NBO Delocalization Energies (kcal mol^{-1}) for Al**1**−Al**3** Stationary Points at Various Levels of Theory

		relative energy[a]				
structure	no. of ν_{imag}	B3LYP	MP2	CCSD(T)// B3LYP	CCSD(T)// MP2	E_{deloc}
Al**1***ip*	0	0.0	0.0	0.0	0.0	0.0
Al**1***op*	1	11.6	11.6	11.8	11.8	10.8
Al**2**ip^{2}	0	0.0	0.0	0.0	0.0	0.0
Al**2**$ipop^{b}$	1	6.5	6.7	6.7	6.7	12.1
Al**2**$op^{2\ b}$	2	18.5	18.8	18.9	18.8	21.7
Al**3**$ip^{3\ c}$	0	0.0				0.0
Al**3**$ip^{2}op$	1	3.9				12.1
Al**3**$ipop^{2\ b}$	2	11.5				24.0
Al**3**op^{3}_{sym}	3	25.3				31.8
Al**3**op^{3}_{asym}	3	25.9				31.5

[a] All energies computed with 6-311+G(2df,p) basis set and reported relative to isomeric local minimum. [b] See corresponding footnote to Table 3. [c] See corresponding footnote to Table 3.

Al1−Al3. The Al−N bond lengths for structures Al**1**−Al**3** are reported in Table 3, and their energetics and NBO delocalization energies are reported in Table 4. There are some significant differences between the structures and energetics of the Al**1**−Al**3** aluminum compounds and those of the corresponding B**1**−B**3** boron compounds.

As is the case for B**1**, the preferred conformation for Al**1** is Al**1***ip*. The Al−N bond length in the Al**1***ip* structure is 1.773 Å (B3LYP) or 1.776 Å (MP2), longer than the B−N bond length in B**1***ip*, which is expected insofar as aluminum

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has a larger covalent radius than boron. These Al−N bond lengths agree nicely with previous computational studies where bond lengths ranging from 1.771 to 1.793 Å have been reported.[13,19,21,23,67−69] Upon rotation of the amino group to the Al**1***op* structure, the Al−N bond length does increase, but by only 0.021 Å (compared to 0.079 Å in the B**1** structure), and the rotational barrier is a mere 11.8 kcal mol^{-1} (compared to 32.1 kcal mol^{-1} in the B**1** structure).

Reported computational rotational barriers for the Al**1** structure[13,19,21,23,68,69] range from 11.2 to 12.6 kcal mol^{-1}, in agreement with the values reported in Table 4 (all levels of theory in the table are in excellent agreement with one another). The majority of these barriers seem to be for the barrier between Al**1***ip* and an Al**1** structure in which the nitrogen has been rotated out-of-plane, but has not been allowed to pyramidalize (a second-order saddle point, Al**1***op-pl*). However, this detail has little quantitative significance because the *op* amino group of the Al**1***op* structure is only weakly pyramidalized: the largest difference in energy between Al**1***op-pl* and the Al**1***op* structure is only 0.1 kcal mol^{-1} at the MP2 level of theory (not shown in table). Experimental barriers to rotation around the Al−N bond of substituted monoaminoalanes have been reported at 9.4 and 9.9 kcal mol^{-1}.[70,71] One would expect the computed rotational barriers to be larger than the experimental ones if sterics contribute to a significant reduction in the barrier heights, since the computations ignore substituent effects. This effect does not seem to be quantitatively large, although experimental structures usually have torsion angles about the Al−N bond that are not equal to zero. Again, the computational model barrier may also be slightly higher than the experimental ones due to favorable electrostatic interactions between the hydrogens of opposite charge on the aluminum and nitrogen, and due to maximum pi bonding in the Al**1***ip* structure.

The idea that the trends in bond lengths of the aminoalanes are due to ionic effects rather than pi bonding is supported by the bond lengths reported for the Al**2** and Al**3** structures in Table 3. Though the *ip* structures remain the favored conformations, in comparing these structures for Al**1**, Al**2**, and Al**3**, it can be seen that the Al−N bond lengths do not change much at all (1.773 Å, Al**1***ip*; 1.776 Å, Al**2***ip*^{2}; 1.778 Å, Al**3***ip*^{3}). If pi bonding was of significant importance, it would be expected that the Al−N bonds would have a more dramatic increase upon addition of a greater number of amino groups (as in the case of the aminoboranes), due to weaker pi bonds.

Upon rotation of the first Al**2** amino group to Al**2***ipop*, the *op* amino group does not pyramidalize, leading to just a single Al**2***ipop* isomer. The *op* Al−N bond length increases by 0.015 Å and the *ip* planar amino Al−N bond length decreases slightly, by 0.004 Å; the barrier to rotation is only 6.7 kcal mol^{-1}. The Al−N bond lengths increase slightly to 1.800 Å each once the second amino group is rotated. However, though these changes are not nearly as dramatic as those seen in the boron system, it is noteworthy that the rotational barriers are still additive after the first amino group is rotated out-of-plane, the same phenomenon that occurs in the boron system.

Results for the Al**3** structure are similar to the Al**2** results. The Al**3***ip*^{3} structure is the lowest energy conformer, with Al−N bond lengths of 1.778 Å. These bond lengths are a bit shorter than those reported for a D_{3h} Al**3***ip*^{3} structure at MP2/6-31+G*, at 1.796 Å,[19] which must be due to the larger basis set since the MP2 bond lengths in Table 3 are in very good agreement with those from B3LYP. The planar Al−N bonds shorten slightly when the first amino group is rotated out-of-plane to the Al**3***ip*^{2}*op* structure. This amino group prefers not to pyramidalize, as with the Al**2** structure, nor does the second amino group pyramidalize when it is rotated out-of-plane to the Al**3***ipop*^{2} structure. The amino groups do pyramidalize when the third amino group is rotated out of plane, however, leading to the Al**3***op*$^{3}_{sym}$ and Al**3***op*$^{3}_{asym}$ isomers. The *ip* Al−N bond is at its shortest distance at 1.770 Å in the Al**3***ipop*^{2} structure, even shorter than in the Al**1***ip* structure, at 1.773 Å. The barrier to rotation of the first amino group is reduced to 3.9 kcal mol^{-1}, at which point the barriers again seem to be additive.

These results for aminoalane compounds support the experimental evidence of a much weaker pi interaction compared to the aminoborane compounds. This interaction is on the order of 12 kcal mol^{-1} when raw energies are evaluated, but when thermal contributions to free energy are included, the monoaminoalane rotational barrier is 9.7 kcal mol^{-1}, in excellent agreement with the 9−10 kcal mol^{-1} upper bound for these systems suggested by the experiments.[1,2,18,19,22,70,71] Of course, one possibility would be that the lower rotational barriers do *not* reflect weaker pi bonding interactions in the minima, but rather much *larger* negative hyperconjugation energies in the TS structures. However, as noted in Table 4, these delocalization energies, which are nearly constant at about 11−12 kcal mol^{-1} per rotated amino group in any structure, are *less* than those computed for the boron system, which are nearly constant at about 13−14 kcal mol^{-1}.

Ga1−Ga3. Theoretical studies have suggested that aminogallane compounds have slightly *stronger* pi interactions than the aminoalanes,[23,68,69] though not nearly as strong as in the aminoboranes. Experimental studies, on the other hand, generally group aminogallanes with the aminoalanes as having similarly weak pi interactions (on the order of 9−10 kcal mol^{-1}) and rationalize changes in bond lengths based on ionic bonding interactions.[1,2] The Ga−N bond lengths computed here for structures Ga**1**−Ga**3** are reported in Table 5, and the energetics and NBO delocalization energies for these structures are reported in Table 6.

The planar Ga**1***ip* structure is the minimum energy conformer, with a Ga−N bond length of 1.822 Å. The

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Table 5. Ga−N Bond Lengths for Structures Ga**1**-Ga**3** Optimized at Various Levels of Theory

	bond lengths (Å)[a]				
	in-plane		out-of-plane		
structure	1	2	1	2	3
	B3LYP/6-311+G(2df,p) Level				
Ga**1***ip*	1.822				
Ga**1***op*	1.883				
Ga**2***ip*^{2}	1.825				
Ga**2***ipop*$_{anti}$	1.827		1.871		
Ga**2***ipop*$_{syn}$	1.819		1.873		
Ga**2***op*$^{2}_{asym}$			1.878	1.887	
Ga**2***op*$^{2}_{sym1}$			1.886		
Ga**2***op*$^{2}_{sym2}$			1.876		
	MP2/6-311+G(2df,p) Level				
Ga**1***ip*	1.886				
Ga**1***op*	1.932				
	B3LYP/CEP1 Level				
Ga**1***ip*	1.823				
Ga**1***op*	1.886				
Ga**2***ip*^{2}	1.823				
Ga**2***ipop*$_{anti}$	1.827		1.873		
Ga**2***ipop*$_{syn}$	1.817		1.874		
Ga**2***op*$^{2}_{asym}$			1.880	1.889	
Ga**2***op*$^{2}_{sym1}$			1.889		
Ga**2***op*$^{2}_{sym2}$			1.878		
Ga**3***ip*^{3}	1.829				
	1.832[b]	1.830[b]			
Ga**3***ip*^{2}*op*	1.826	1.818	1.866		
Ga**3***ipop*$^{2}_{asym}$	1.819		1.872	1.877	
Ga**3***ipop*$^{2}_{sym1}$	1.830		1.869		
Ga**3***ipop*$^{2}_{sym2}$	1.812		1.879		
Ga**3***op*$^{3}_{sym}$			1.885		
Ga**3***op*$^{3}_{asym}$			1.875	1.883	1.897

[a] Only one length is reported when two or more bonds are identical by symmetry. [b] Pyramidalization of the in-plane amino groups creates two stereoisomers of C_{3v} (above) and C_s (below) symmetry.

Table 6. Relative and NBO Delocalization Energies (kcal mol^{-1}) for Ga**1**−Ga**3** Stationary Points at Various Levels of Theory

		relative energy[a]					
structure	no. of ν_{imag}	B3LYP	B3LYP/ CEP1	MP2	CCSD(T)// B3LYP	CCSD(T)// MP2	E_{deloc}/ CEP1
Ga**1***ip*	0	0.0	0.0	0.0	0.0	0.0	0.0
Ga**1***op*	1	13.0	12.8	11.5	10.5	11.2	6.8
Ga**2***ip*^{2}	0	0.0	0.0				0.0
Ga**2***ipop*$_{anti}$	1	7.4	7.3				6.7
Ga**2***ipop*$_{syn}$	1	6.8	6.7				9.3
Ga**2***op*$^{2}_{asym}$	2	19.1	18.9				14.3
Ga**2***op*$^{2}_{sym1}$	2	19.2	18.9				13.0
Ga**2***op*$^{2}_{sym2}$	2	20.1	20.1				14.9
Ga**3***ip*^{3}	0		0.0				0.0
	0[b]		−0.2[b]				0.0[b]
Ga**3***ip*^{2}*op*	1		4.0				7.8
Ga**3***ipop*$^{2}_{asym}$	2		10.9				15.3
Ga**3***ipop*$^{2}_{sym1}$	2		12.3				10.4
Ga**3***ipop*$^{2}_{sym2}$	2		10.4				17.4
Ga**3***op*$^{3}_{sym}$	3		22.1				21.2
Ga**3***op*$^{3}_{asym}$	3		23.3				20.8

[a] All energies are reported relative to the relevant isomeric local minimum and computed with the 6-311+G(2df,p) basis set unless the CEP1 basis is specified. [b] See corresponding footnote to Table 5.

aminogallane compounds are the first structures in this series that seem to have a relatively large difference between the B3LYP and MP2 Ga−N bond distances (1.822 and 1.886 Å, respectively). It is difficult to compare the computational monoaminogallane Ga−N bond length to experimental bond lengths to corroborate one level of theory over the other since the monoaminogallane structures available experimentally have large, bulky substituents on the amino group, which would affect the bond length. The Ga−N bond length obtained with B3LYP is in agreement with those obtained by previous computational studies,[23,68,69] but these were also all obtained with the B3LYP density functional (with differing basis sets). Upon investigating the single-point CCSD(T) energy calculations on both the B3LYP and MP2 optimized structures, the B3LYP structure is 0.7 kcal mol^{-1} lower in energy than the MP2, suggesting that B3LYP yields the better structure. It will be the level of theory of choice for the remaining analyses.

It is also noteworthy that the DFT bond lengths and energies calculated with the CEP1 basis set are in excellent agreement with those calculated with the all-electron 6-311+G(2df,p) basis set. Upon rotation of the amino group to Ga**1***op*, the Ga−N bond length increases by 0.061 Å to 1.883 Å, a larger increase than in Al**1** (0.021 Å), but a smaller increase than in B**1** (0.079 Å). Though the increase in the Ga−N bond length is more similar to the increase in the B**1** compound, the barrier to rotation is less than half that seen with monoaminoborane, at 13.0 kcal mol^{-1}. Initially, these numbers seem to be at odds with those reported in previous computational studies, where the change in bond length upon rotation of the Ga−N bond is approximately 0.03 Å;[23,68,69] however, this is again an issue of allowing the rotated amino group to pyramidalize to the first-order saddle point, Ga**1***op*. The difference in the Ga−N bond length between Ga**1***ip* and Ga**1***op-pl* is 0.033 Å, in agreement with prior studies. The difference in energy between the Ga**1***op* structure and Ga**1***op-pl* is about 1.0 kcal mol^{-1}, indicative of a moderately flat potential energy surface coupling the bond length and pyramidalization coordinates.

This trend continues for the Ga**2** and Ga**3** structures. The changes in Ga−N bond lengths are consistently between the aminoborane and aminoalane values, and the rotational barriers are similar to the aminoalane barriers, but slightly higher. There are several differences between the aminoalane and aminogallane structures. The aminogallane *op* amino groups pyramidalize, leading to the existence of isomers related by inversion of the amino groups, which makes them more similar to the aminoborane structures. Another subtle difference that has not been seen in either the aminoborane or -alane structures is that the Ga**3***ip*^{3} structure prefers pyramidal amino groups to planar ones. It seems evident that there is very little pi bonding interaction, then, between Ga and any individual amino group: the barrier to rotation of the first amino group to the Ga**3***ip*^{2}*op* structure is only 4.0 kcal mol^{-1}. Again, it is seen by the NBO delocalization energies in Table 6 that there is no dependence on the orientation of the pyramidalized group(s), and the energies are additive with a factor of about 7−8 kcal mol^{-1} per rotated amino group. Note that this delocalization energy per amino group is *smaller* than in the aminoalane systems. Thus, to the extent that rotational energies are somewhat higher in the Ga molecules than their Al analogues, this appears *not* to be due to increased pi bonding interactions, but rather to *decreased* stabilization of the TS structures by negative hyperconjugation. If anything, the pi bonding in the Ga case

Table 7. In−N Bond Lengths for Structures In**1**−In**3** Optimized at Various Levels of Theory

	bond lengths (Å)[a]				
	in-plane		out-of-plane		
structure	1	2	1	2	3
	B3LYP/CEP1 Level				
In**1***ip*	2.039				
In**1***op*	2.108				
In**2***ip*^{2}	2.049				
	2.050[b]				
In**2***ipop*$_{anti}$	2.043		2.093		
In**2***ipop*$_{syn}$	2.032		2.093		
In**2***op*$^{2}_{asym}$			2.101	2.112	
In**2***op*$^{2}_{sym1}$			2.112		
In**2***op*$^{2}_{sym2}$			2.099		
In**3***ip*^{3}	2.056				
	2.057[c]	2.057[c]			
In**3***ip*^{2}*op*	2.048	2.058	2.089		
In**3***ipop*$^{2}_{asym}$	2.035		2.090	2.100	
In**3***ipop*$^{2}_{sym1}$	2.047		2.088		
In**3***ipop*$^{2}_{sym2}$	2.025		2.099		
In**3***op*$^{3}_{sym}$			2.107		
In**3***op*$^{3}_{asym}$			2.095	2.105	2.120
	MP2/CEP1 Level				
In**1***ip*	2.017				
In**1***op*	2.077				
	B3LYP/CEP2 Level				
In**1***ip*	2.029				
In**1***op*	2.109				
In**3***ip*^{3}	2.063[d]				
In**3***ip*^{2}*op*	2.052	2.064	2.097		
In**3***ipop*$^{2}_{asym}$	2.029		2.096	2.106	
In**3***ipop*$^{2}_{sym1}$	2.041		2.095		
In**3***ipop*$^{2}_{sym2}$	2.019		2.106		
In**3***op*$^{3}_{sym}$			2.112		
In**3***op*$^{3}_{asym}$			2.099	2.110	2.125

[a] Only one length is reported when two or more bonds are identical by symmetry. [b] Pyramidalization of the in-plane amino groups creates two stereoisomers of C_2 (above) and C_s (below) symmetry. [c] See footnote *b* to Table 5. [d] The pyramidalized C_s structure converts without barrier to the pyramidalized C_{3v} structure.

Table 8. Relative and NBO Delocalization Energies (kcal mol^{-1}) for In**1**−In**3** Stationary Points at Various Levels of Theory

		relative energy[a]					
structure	no. of ν_{imag}	B3LYP	B3LYP/ CEP2	MP2	CCSD(T)// B3LYP	CCSD(T)//MP 2	E_{deloc}
In**1***ip*	0	0.0	0.0	0.0	0.0	0.0	0.0
In**1***op*	1	9.0	9.0	9.9	9.6	9.7	4.6
In**2***ip*^{2} [b]	0	0.0					0.0
	0	0.1					0.0
In**2***ipop*$_{anti}$	1	5.1					4.3
In**2***ipop*$_{syn}$	1	4.9					6.5
In**2***op*$^{2}_{asym}$	2	13.1					10.1
In**2***op*$^{2}_{sym1}$	2	12.9					8.5
In**2***op*$^{2}_{sym2}$	2	14.1					10.3
In**3***ip*^{3}	0	0.0	0.0				0.0
	0[c]	−0.1[c]	0.0[c]				0.0[c]
In**3***ip*^{2}*op*	1	3.3	2.6				5.9
In**3***ipop*$^{2}_{asym}$	3	8.1	7.0				11.4
In**3***ipop*$^{2}_{sym1}$	3	9.0	8.3				9.5
In**3***ipop*$^{2}_{sym2}$	3	7.7	6.7				11.9
In**3***op*$^{3}_{sym}$	3	15.1	13.3				16.0
In**3***op*$^{3}_{asym}$	3	15.9	14.5				14.5

[a] All energies are reported relative to the relevant isomeric local minimum and computed with the CEP1 basis set unless otherwise specified. [b] See corresponding footnote to Table 7. [c] See footnote *b* to Table 5.

would appear to be slightly *weaker* than in the Al case, consistent with previous experimental inferences.

The available experimental rotational energies for aminogallanes are 9.7,[70] 10.1,[18] and 17.0[72] kcal mol^{-1} for substituted monoaminogallanes (sterics are expected to play a large role in the barrier of the last case) and 9−10[1] kcal mol^{-1} for a substituted diaminogallane. Once thermal contributions to free energy are included in the computed monoaminogallane rotational barrier, it is decreased to 11.8 kcal mol^{-1}, a barrier slightly higher than predicted by experiment. This low rotational barrier, along with the observation that the Ga−N bond lengths of the planar structures do not increase upon additional amino substitution (1.823 Å, Ga**1***ip*; 1.823 Å, Ga**2***ip*^{2}; 1.829 Å, Ga**3***ip*^{3}), supports the experimental assignment of a much weaker pi interaction in aminogallanes than aminoboranes.

In1−In3. The In−N bond lengths for structures In**1**−In**3** are reported in Table 7, and their energetics and NBO delocalization energies are reported in Table 8. The In**1***ip* structure has an In−N bond length of 2.039 Å, which increases by 0.069 Å to 2.108 Å when the amino group is rotated to the In**1***op* structure. This increase is in fair agreement at all three levels of theory, and is similar to the increase seen in Ga**1**. The In−N bond length is a bit larger than that reported in a previous study,[68,69] which is probably attributable to different indium basis sets (CEP vs LanL2DZ). The change in bond length upon rotation of the amino group to the In**1***op-pl* structure with the CEP1 basis set (0.029 Å, not tabulated) is, however, in agreement with the change reported in that study (0.028 Å). The rotational barrier from In**1***ip* to In**1***op* is 9.0 kcal mol^{-1}, the lowest barrier seen in this series of monoamino compounds. The barrier heights computed at MP2 (9.9 kcal mol^{-1}) and CCSD(T)//X (X = B3LYP, 9.6 kcal mol^{-1}; X = MP2, 9.7 kcal mol^{-1}) are very slightly higher than that calculated with B3LYP, but still lower than any of the other monoamino rotational barriers reported. The value for the rotational barrier of the monoaminoindane previously reported, 12.3 kcal mol^{-1},[68,69] is the difference in energy between the In**1***ip* structure and the In**1***op-pl* structure. The value for that barrier using CEP1 is in fair agreement at 11.3 kcal mol^{-1} (not tabulated). In**1***op* also has the lowest NBO delocalization energy of the monoamino series, a mere 4.6 kcal mol^{-1}, but this is consistent with it having the longest X−N bond length and the poorest overlap of relevant orbitals.

The In**2***ip* and In**3***ip* structures are similar to the Ga**3***ip* structure in that they prefer pyramidal amino groups over planar. It is evident that the energy cost required to planarize the amino groups (on the order of 5−6 kcal mol^{-1} for ammonia[73,74]) outweighs the improved pi conjugation energy for that conformation. The balance is close, however, given that the In**2***ip*^{2} geometry in which the amino groups are forced to be planar is only 0.4 kcal mol^{-1} higher in energy than the C_2 structure. While the amino groups are not planar, there is still a weak pi interaction. The energy required to rotate the first amino group to the In**2***ipop*$_{anti}$ or In**2***ipop*$_{syn}$

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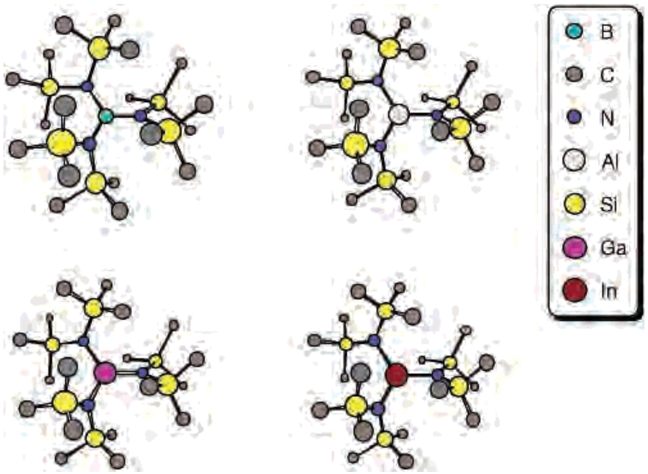

Figure 2. Ball-and-stick structures for $[(Me_3Si)_2N]_3X$, X = B, Al, Ga, In (see Computational Methods section for computational details). Hydrogen atoms have been removed for clarity.

structure is on the order of 5 kcal mol^{-1}. The NBO delocalization energy is again seen to be generally constant at 4−5 kcal mol^{-1} with no significant dependence on the orientation of the lone pair of the amino group, and the energetics for rotation of amino groups are additive for this final metal of the series as well.

A similar story is predicted for the In**3** compounds. Rotation of the first amino group to the In**3***ip*^{2}*op* structure requires only 3.3 kcal mol^{-1}, a very low barrier indeed. Rotational barriers in In**3** continue to be additive. One point of note with the In**3***ipop*^{2} conformers is that they all have three imaginary frequencies rather than two as was seen with the boron, aluminum, and gallium compounds. This is due to the pyramidalization of the *ip* nitrogens, which makes the second-order saddle points C_1, and quite difficult to find given the very flat nature of the potential energy surface along various coordinates. However, the use of the third-order saddle point energies should be an eminently acceptable approximation given that there is a mere 0.4 kcal mol^{-1} energy difference between the In**2***ip*^{2} structures having planar vs pyramidal amino groups.

Besides pyramidal amino groups in the planar conformations and low rotational barriers, another feature indicative of very weak pi interactions in the aminoindanes is the general consistency of the In−N bond lengths in the planar In**1**−In**3** structures upon the addition of amino groups (2.039 Å, In**1***ip*; 2.049 Å, In**2***ip*^{2}; 2.056 Å, In**3***ip*^{3}). Experimental data available for a substituted monoaminoindane[20] have been interpreted to indicate an In−N rotational barrier with an upper limit of 8−9 kcal mol^{-1}. This number is in excellent agreement with the computed rotational barrier for monoaminoindane, which is 8.5 kcal mol^{-1} after thermal contributions to free energy are included.

TMS-Substituted Systems. Calculations were also performed on the TMS-substituted amino systems $X[N(SiMe_3)_2]_3$, X = B, Al, Ga, In (Figure 2). The relevant geometrical data are reported in Table 9 along with the experimental data (crystal structures are available for three of the four structures: aluminum,[75] gallium,[18] and indium.[20]). The geometries of all four compounds are largely insensitive to the central metal atom, other than a general increase in the X−N bond length, which is to be expected with the increase in atomic number. The computed X−N bond lengths are in fair to good agreement with experiment, being consistently overestimated, perhaps because of basis set limitations imposed by the large size of these systems. Remaining geometrical parameters are in excellent agreement with experiment.

Table 9. Geometrical Data for TMS-Substituted Systems: $X[N(SiMe_3)_2]_3$

X	X−N (Å)	N−Si (Å)	Si−N−Si (deg)	torsion angle[a] (deg)
B	1.490	1.801	113.8	46.4
Al	1.844	1.780	118.2	48.4
exptl[b]	1.78	1.75	118	50.0
Ga	1.886	1.779	119.7	49.5
exptl[c]	1.868	1.743	120.2	48.6
In	2.102	1.768	122.6	49.4
exptl[d]	2.049	1.739	122.7	48.6

[a] Angle between perpendiculars to the XN_3 and NSi_2 planes. [b] Reference 75. [c] Reference 18. [d] Reference 20.

Experimental N−Si distances, Si−N−Si angles, and torsion angles all fall within very narrow ranges: 1.739−1.75 Å, 118−122.7°, and 48.6−50.0°, respectively. Similar ranges are seen for the computed values: 1.768−1.780 Å, 118.2−122.6°, and 48.4−49.5°, respectively. Interestingly, the boron derivative, while not known experimentally, is predicted to have a very similar geometry except for much shorter bond lengths to the central main-group atom. It is evident, then, that steric interactions of the TMS groups completely dominate the geometries of these molecules, without influence from differential pi bonding effects.

Some Final Observations. One apparently curious anomaly in the trends observed as a function of group 13 central atom is the manner in which rotated amino groups in the various alanes tend to remain planar even though they are inevitably pyramidal in the analogous boranes, gallanes, and indanes. We suggest that this is a manifestation of Bent's rule[76] arising as a consequence of the differing electronegativities of the group 13 atoms. Put succinctly, Bent's rule states that the nitrogen atom will employ more s character in its hybrid orbital contribution to the X−N σ bonding orbital as the group 13 atom X becomes less electronegative. Increased s character in the bonding orbital will reduce s character to the lone pair and thereby lower the barrier to inversion of the amino group. If we examine the inversion barriers on going from C_s **1***op* to C_{2v} **1***op-pl* at the CCSD(T)//DFT level of theory, they are 4.2, 0.04, 1.2, and 1.7 kcal mol^{-1}, respectively, for B, Al, Ga, and In. These same atoms have Pauling electronegativities[77] as determined by Allred[78] of 2.04, 1.61, 1.81, and 1.78, respectively. The Pearson correlation coefficient *R* between the inversion barriers and the electronegativities is 0.976. While it is not a priori obvious that one should expect a linear relationship between these

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quantities, the correlation does provide qualitative support for the invocation of Bent's rule. Further support derives from investigation of the X−N NBOs. The nitrogen hybrid contribution to the Al−N orbital in **1***op-pl* is predicted at the DFT level to have 52.8% p character, the lowest percentage of p character (and hence the highest of s character) of any of the four **1***op-pl* analogues.

Finally, Rissler et al.[79] recently presented a theoretical study of pnicogen-substituted carbenium and silicenium ions, including the triamino cases isoelectronic with B**3** and Al**3** (note that the carbenium ion is better known as the guanidinium cation). While they did not consider rotational TS structures, it is still interesting to compare features of the corresponding equilibrium structures. The X−N bond lengths for the compounds with group 14 central atoms are 0.1−0.12 Å shorter than those found in the corresponding group 13 analogues, reflecting the much more aggressive π-acceptor characteristics of the cationic group 14 atoms compared to the neutral group 13 atoms. Curiously, although the amino groups in all four cases are perfectly planar, in the compounds having group 14 central atoms these groups prefer to rotate slightly so that the symmetry of the equilibrium structure is reduced from D_{3h} to D_3. While in the guanidinium ion one might be tempted to assign this to steric congestion given C−N bond lengths of 1.335 Å,[79] it does not seem reasonable to invoke the same congestion in the silicenium analogue, where the Si−N bond lengths are a comfortable 1.657 Å (much longer than the B−N bond lengths in D_{3h} B**3***ip*). This puzzle's solution is left to those inclined to ponder upon it.

Conclusions

A systematic study of mono-, di-, and triaminoborane, -alane, -gallane, and -indane shows that pi bonding plays a significant role in the structures and energetics of aminoborane compounds, but a much less energetically significant role in the others. There are some subtle differences in the conformations of the amino substituents depending on the central group 13 metal. When attached to boron, in-plane amino groups prefer to be planar and out-of-plane amino groups prefer to pyramidalize, leading to isomers related by inversion. When attached to aluminum, in-plane amino groups prefer to be planar, but out-of-plane amino groups generally prefer not to pyramidalize, leading to fewer isomeric conformers. Amino groups attached to gallium exhibit similar preferences as when boron is the central atom, except for triaminogallane, where reduced pi bonding to any one amino group causes all three in-plane amino groups to be pyramidal. This phenomenon is also observed in di- and triaminoindane, indicating very weak pi interactions for these compounds too. NBO delocalization energies reveal that negative hyperconjugation is an important interaction when the amino groups are rotated out of plane; however, there is no preference for $n \rightarrow \sigma^*_{X-N}$ interactions over $n \rightarrow \sigma^*_{X-H}$ interactions. Thus, for each of the group 13 metals investigated, the energy required to rotate successive amino groups after the first can be computed in an additive fashion using data from less substituted systems. An investigation of the TMS-substituted systems indicates that these structures are little affected by the choice of the central metal atom.

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