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σ- and π-Bond Strengths in Main Group 3−5 Compounds

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The σ- and π-bond strengths for the molecules BH_2NH_2, BH_2PH_2, AlH_2NH_2, and AlH_2PH_2 have been calculated by using ab initio molecular electronic structure theory at the CCSD(T)/CBS level. The adiabatic π-bond energy is defined as the rotation barrier between the equilibrium ground-state configuration and the $C_s$symmetry transition state for torsion about the A−X bond. We also report instrinsic π-bond energies corresponding to the adiabatic rotation barrier corrected for the inversion barrier at N or P. The adiabatic σ-bond energy is defined as the dissociation energy of AH_2XH_2 to $AH_2 + XH_2$ in their ground states minus the adiabatic π-bond energy. The adiabatic σ-bond strengths for the molecules BH_2NH_2, BH_2PH_2, AlH_2NH_2, and AlH_2PH_2 are 109.8, 98.8, 77.6, and 68.3 kcal/mol, respectively, and the corresponding adiabatic π-bond strengths are 29.9, 10.5, 9.2, and 2.7 kcal/mol, respectively.

Introduction

The suitability of NH_xBH_x ($x = 1-4$) compounds for hydrogen storage has recently been evaluated using theoretical methods.[1−3] The calculations showed that BH_3NH_3(g), BH_3NH_3(s), and $[BH_4^-][NH_4^+]$(s) can potentially serve as hydrogen storage systems based on the thermodynamics. In addition, molecular systems isoelectronic to the amine boranes were studied computationally as alternative candidates for H_2 storage systems.[4] On the basis of the calculated heats of formation, AlH_3NH_3(g), $[AlH_4^-][NH_4^+]$(s), AlH_3PH_3(g), $[AlH_4^-][PH_4^+]$(s), and $[BH_4^-][PH_4^+]$(s) have the potential to serve as H_2 storage systems in terms of the reaction energetics for H_2 release.

We are interested in the chemistry of these species in terms of their stability and reactivity. Because of the novel electronic structure of these species, we are interested in their bond energies. We previously have provided the best estimates of the Lewis acid−base donor−acceptor σ-bond strengths in AH_3XH_3 compounds as shown in Table 1.[3,4] These values are quite low as compared to a covalent C−C σ-bond energy, for example, the value of 90.1 kcal/mol at 298 K for C_2H_6.[5] The AH_3XH_3 molecules can eliminate H_2 to form AH_2XH_2 molecules. The resulting AH_2XH_2 molecules have σ-bonds formed between the AH_2 and XH_2 groups with approximate sp^2-sp^2 hybridization and π-bonds formed by donation of the lone pair on the Group VA XH_2 group to the vacant p orbital on the Group IIIA AH_2 group. The strengths of the π-bond and the resulting σ-bond are questions that need to be addressed. We are particularly interested in the inherent bond energies of the σ- and π-bonds to better understand the thermodynamic driving forces for H_2 release. The bond energies in these systems can be compared to the σ- and π-bond strengths in C_2H_4, which has a covalent π bond.[6]

Several methods exist in the literature for determining π-bond strengths. A general procedure is to compare the bond dissociation energies of double, $D°(X = Y)$, and single, $D°(X-Y)$, bonds. The issue here is the proper description of how to define the π-bond energy.[7−9] One method involves the use of hydrogenation thermochemical cycles and bond dissociation energies. The energy required to dehydrogenate a singly bonded compound to produce a double bond can be used to estimate the strength of the double bond provided that the overall heat of the dehydrogenation reaction and the bond dissociation energies are known.[6,10] One also can look at the barrier to rotation about the A−X bond as rotation about the σ-bond by 90° breaks the π-bond interaction of the molecule. This can be done, for example, by measuring the kinetics for cis−trans isomerization.[11] Borden[7] has discussed various approaches to calculating the π-bond energy in olefins and has shown that relaxation of the orthogonal diradical is important in determining the π bond energy in C_2F_4 as compared to C_2H_4 as well as issues related to diabatic (dissociation to the configuration most closely representing the bonding configuration in the molecule) vs adiabatic (dissociation to the ground state of the separated species) dissociation energies. Carter and Goddard have provided a similar discussion for substituted olefins.[8]

TABLE 1: Donor σ-bond Strengths in AH_3XH_3 Compounds[a]

molecule	σ-bond energy (0 K)	σ-bond energy (298 K)
H_3BNH_3[b]	25.9	27.2
H_3AlNH_3[c]	26.1	27.3
H_3BPH_3[c]	21.1	22.5
H_3AlPH_3[c]	14.0	14.7

[a] In kcal/mol. [b] Ref 3. [c] Ref 4.

To calculate the σ-bond energy, one has to evaluate the π bond strength. We have chosen to use the rotation barrier approach as the hydrogenation method could lead to very different types of radicals than those found in carbon-based systems, and it is not possible to determine which end to hydrogenate first. We can write the following process:

$$H_2A = XH_2 \rightarrow {}^{\bullet}AH_2 + {}^{\bullet}XH_2 \qquad \Delta H\,(0\ \mathrm{K}) = \sigma\text{-bond} + \pi\text{-bond} \quad (1)$$

where A is the Group 3A atom and X is the group 5A atom. The total dissociation energy for this reaction is the sum of the σ- and π-bond energies. Given the energies of the three species,

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one can calculate the sum of the σ- and π-bond energies. The sum of the bond energies at the adiabatic limit is for dissociation to the ground states, which are $^2A_1$ for AH_2 (orbital with unpaired electron in the plane) and $^2B_1$ for XH_2 (orbital with unpaired electron out of the plane and orbital with the lone pair in the plane). To calculate the π bond energy, one can rotate about the A−X bond by 90° so that there is no interaction between the lone pair on the XH_2 with the vacant orbital on AH_2.

$$H_2A = XH_2 \rightarrow H_2A - XH_2 \qquad \Delta H\,(0\text{ K}) = \pi\text{-bond} \quad (2)$$

In C_2H_4, this is equivalent to breaking the covalent interaction between the p orbitals and to putting one electron on each CH_2 group to form a diradical. For the Group 3−5 binary compounds $H_2A = XH_2$ with A = B, Al and X = N, P the rotation process stays on the closed shell singlet potential energy surface so that there is no need to be concerned with accessing an open shell species. In the rotated structure, the pair of electrons involved in the rotation localize as the lone pair on the Group 5A atom. An issue that arises in these compounds is the structure in the rotated state.

There have been several previous theoretical studies of the σ- and π-bond energies of the molecules presented here. Allen and Fink[12] predicted that aminoborane, BH_2NH_2, has two rotational transition states at the CISD+Q/DZ+P level, one of C_s symmetry at 32.4 kcal/mol and one of C_{2v} symmetry at 37.9 kcal/mol, both with respect to the planar ground-state configuration. This type of energy difference is consistent with relaxation of the geometry in the rotated structure as discussed by Borden[7] as well as the size of the inversion barrier in NH_3.[13] McKee[14] predicted the rotational barrier in BH_2NH_2 to be 32.1 kcal/mol at the MP4/6-31+G(2d,p) level of theory. Allen et al.[15] and Allen and Fink[16] also investigated the internal rotational energy barrier of borylphosphine at the level described above. They predicted that the BH_2PH_2 molecule can undergo internal rotation through either a low-energy transition state of C_s symmetry 10.0 kcal/mol above the ground-state structure or a high-energy transition state of C_{2v} symmetry, 46.4 kcal/mol above the ground state. The difference in the two rotation barriers is consistent with the inversion barrier in PH_3.[17] Coolidge and Borden[18] also have studied the rotation barrier in BH_2PH_2 and found a barrier of 10.4 kcal/mol passing through a C_s transition state and a barrier of 44.6 kcal/mol passing through a C_{2v} rotated structure at the MP4 level. For alane amine, AlH_2NH_2, Fink et al.[19] predicted the rotational energy barrier to be 11.2 kcal/mol at the RHF/6-31+G** level. Davy and Jaffrey[20] obtained a value of 11.0 kcal/mol for the rotational barrier energy of AlH_2NH_2 at the HF/DZP level.

We use the approach developed for accurate molecular thermochemistry[21] and for the heats of formation of the parent compounds[3,4] to predict the bond energies. This approach is based on calculating the total atomization energy of a molecule and using this with known heats of formation of the atoms to calculate the heat of formation at 0 K. The approach starts with the coupled cluster theory with single and double excitations and includes a perturbative triples correction (CCSD(T)),[22−24] combined with the correlation-consistent basis sets[25,26] extrapolated to the complete basis set limit to treat the correlation energy of the valence electrons. This is followed by a number of smaller additive corrections including core−valence interactions and relativistic effects, both scalar and spin−orbit. Finally, one must include the zero point energy obtained either from experiment, theory, or some combination. Corrections to 298 K then can be calculated by using standard thermodynamic and statistical mechanics expressions in the rigid rotor-harmonic oscillator approximation[27] and appropriate corrections for the heat of formation of the atoms.[28]

Computational Approach

We used the augmented correlation consistent basis sets aug-cc-pV*n*Z for H, B, and N (*n* = D, T, Q).[25,26] For the sake of brevity, we abbreviate the names to aV*n*Z. Only the spherical components (5d, 7f, and 9g) of the Cartesian basis functions were used. All of the current work was performed with the MOLPRO suite of programs.[29] The open-shell CCSD(T) calculations for the atoms were carried out at the R/UCCSD(T) level. In this approach, a restricted open shell Hartree−Fock (ROHF) calculation was initially performed and the spin constraint was relaxed in the coupled cluster calculation.[30−32] All of the calculations were done on a massively parallel HP Linux cluster with 1970 Itanium-2 processors in the Molecular Sciences Computing Facility in the William R. Wiley Environmental Molecular Sciences Laboratory or on the 144 processor Cray XD-1 computer system at the Alabama Supercomputer Center.

The geometries were optimized numerically at the frozen core CCSD(T) level with the aug-cc-pVDZ and aug-cc-pVTZ correlation-consistent basis sets. The CCSD(T)/aug-cc-pVTZ geometries were then used in single point CCSD(T)/aug-cc-pVQZ calculations. For the planar and rotated C_{2v} structures, geometry optimizations only were done at the CCSD(T)/aug-cc-pVDZ level as the energies of the ground state structure or the lowest energy rotated structure only decreased by a few tenths of a kcal/mol upon optimization at the CCSD(T)/aug-cc-pVTZ level. All of the vibrational frequencies were calculated at the MP2/cc-pVTZ level[33] using the Gaussian program system.[34] These were used for the zero point energies and for the thermal corrections and entropies.

It recently has been found that tight d functions are necessary for calculating accurate atomization energies for 2nd row elements,[35] so we also included additional tight d functions in our calculations. Basis sets containing extra tight d functions are denoted aug-cc-pV(*n*+d)Z in analogy to the original augmented correlation consistent basis sets. We use aug-cc-pV(*n*+d)Z to represent the combination of aug-cc-pV(*n*+d)Z (on the 2nd row atoms Al and P) and aug-cc-pV*n*Z (on H, B, and N) basis sets and abbreviate this as aV(*n*+d)Z. The CCSD(T) total energies were extrapolated to the CBS limit by using a mixed exponential/Gaussian function of the form:

$$E(n) = E_{\text{CBS}} + A\exp[-(n-1)] + B\exp[-(n-1)^2] \quad (3)$$

with $n = 2$ (DZ), 3 (TZ) and 4 (QZ), as first proposed by Peterson et al.[36] This extrapolation method has been shown to yield atomization energies in the closest agreement with experiment (by a small amount) as compared to other extrapolation approaches up through $n = 4$.

Core-valence corrections, ΔE_{CV}, were obtained at the CCSD(T)/cc-pwCVTZ level of theory.[37] Scalar relativistic corrections (ΔE_{SR}), which account for changes in the relativistic contributions to the total energies of the molecule and the constituent atoms, were included at the CI−SD (configuration interaction singles and doubles) level of theory using the cc-pVTZ basis set. ΔE_{SR} is taken as the sum of the mass-velocity and 1-electron Darwin (MVD) terms in the Breit-Pauli Hamiltonian.[38] Most calculations using available electronic structure computer codes do not correctly describe the lowest energy spin multiplet of an atomic state as spin−orbit in the atom is usually not included. Instead, the energy is a weighted average of the available multiplets. For N or P in the ^4S state, no spin−orbit correction

TABLE 2: Optimized CCSD(T) Bond Lengths (Å) and Bond Angles (°) for the Rotated Structures of AH_2XH_2 in C_s and C_{2v} Symmetries

molecule	basis set	R_{XH}	∠HXH	∠HXA	R_{AH}	∠HAH	∠HAX	R_{XA}
BH_2NH_2(rot)	aVDZ	1.0308	101.34	108.25	1.2172	118.63	122.22	1.4912
	aVTZ	1.0218	101.86	108.87	1.2032	118.58	122.12	1.4793
BH_2NH_2(rot-planar)	aVDZ	1.0124	113.64	123.18	1.2475	117.36	121.32	1.4735
BH_2PH_2(rot)	aVDZ	1.4418	90.76	91.85	1.2067	119.00	120.77	1.9813
	aVTZ	1.4277	90.71	91.87	1.1920	119.13	120.62	1.9627
BH_2PH_2(rot-planar)	aVDZ	1.4009	115.20	122.40	1.2044	119.65	120.17	1.9646
AlH_2NH_2(rot)	aVDZ	1.0222	105.84	118.61	1.5967	119.17	122.67	1.8491
	aVTZ	1.0110	107.37	122.35	1.5899	118.44	122.37	1.8066
AlH_2NH_2(rot-planar)	aVDZ	1.0163	109.18	125.41	1.5937	118.68	120.66	1.8313
AlH_2PH_2(rot)	aVDZ	1.4417	91.84	90.46	1.5933	119.77	120.74	2.3924
	aVTZ	1.3971	91.71	90.02	1.5867	119.55	120.77	2.3645
AlH_2PH_2(rot-planar)	aVDZ	1.4073	109.18	125.41	1.5868	119.98	120.01	2.3227

TABLE 3: Calculated Imaginary Vibrational MP2/(cc-pVTZ) Frequencies (cm^{-1})

molecule	symmetry	calcd	type
BH_2NH_2 rot	a″	778.9i	rotation
BH_2PH_2 rot	a″	393.1i	rotation
AlH_2NH_2 rot	a″	516.2i	rotation
AlH_2PH_2 rot	a″	186.5i	rotation
BH_2NH_2 rot-planar	a_2	1186.2i	rotation
	b_2	631.5i	inversion
BH_2PH_2 rot-planar	a_2	1150.7i	rotation
	b_2	870.7i	inversion
AlH_2NH_2 rot-planar	a_2	549.3i	rotation
	b_2	164.2i	inversion
AlH_2PH_2 rot-planar	b_2	641.8i	inversion
	a_2	532.7i	rotation

is needed, but a correction of 0.03 kcal/mol is needed for B and one of 0.21 kcal/mol for Al, taken from the excitation energies of Moore.[39]

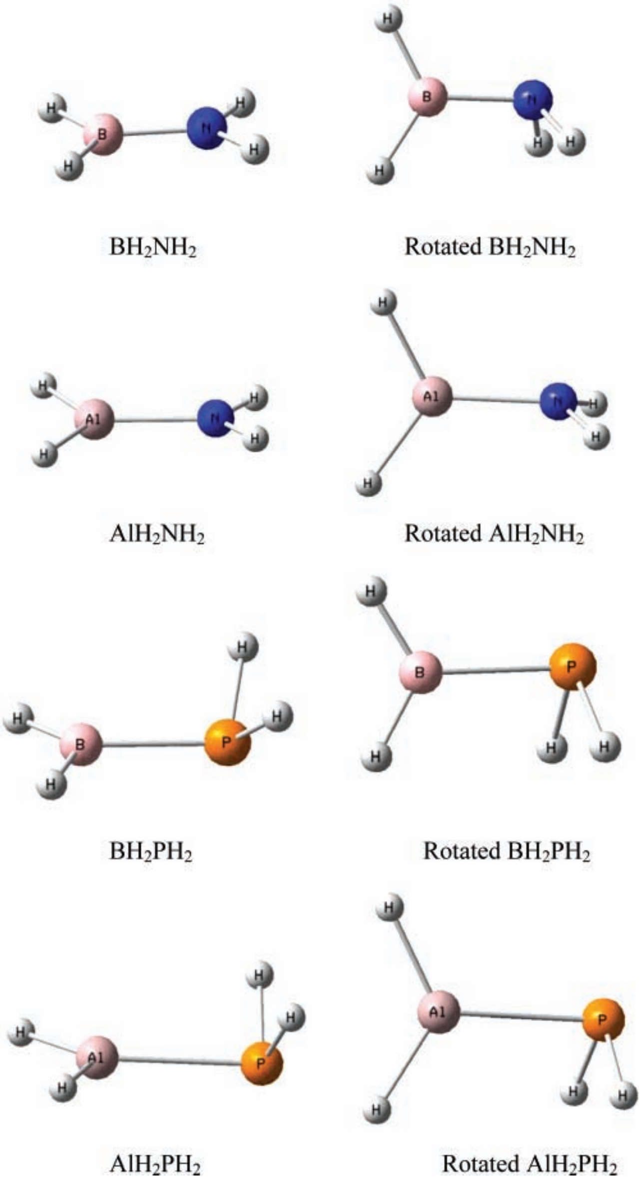
To calculate the zero point energy correction, we scaled the M−H frequencies by the factors 0.96 for M = B and M = N, 0.95 for M = P, and 0.954 for M = Al. These scale factors were obtained by taking the average of the CCSD(T)/aug-cc-pVTZ values and the experimental values for the M−H stretches for the MH_3 compounds and dividing them by the MP2/cc-pVTZ value. Thus we estimate that the error introduced in the heats of formation due to the zero point energies is a maximum of ±0.5 kcal/mol.

By combining our computed ΣD_0 (total atomization energies) values with the known heats of formation at 0 K for the elements $\Delta H_f^0(N) = 112.53 \pm 0.02$ kcal mol^{-1}, $\Delta H_f^0(B) = 136.2 \pm 0.2$ kcal mol^{-1}, $\Delta H_f^0(P) = 75.42 \pm 0.24$ kcal mol^{-1}, $\Delta H_f^0(Al) = 78.23 \pm 1.0$ kcal mol^{-1}, and $\Delta H_f^0(H) = 51.63$ kcal mol^{-1},[40] we can derive ΔH_f^0 values for the molecules under study in the gas phase. We obtain heats of formation at 298 K by following the procedures outlined by Curtiss et al.[28]

Results and Discussion

The calculated geometries of the orthogonal transition state structures, corresponding to rotation about the AX bond, and the C_{2v} structures obtained by rotating about the A−X bond and planarizing the AH_2 and XH_2 groups are given in Table 2. In addition, structures for planar NH_3 and PH_3 and the triatomic molecules BH_2, AlH_2, and PH_2 are provided as Supporting Information. The calculated vibrational frequencies for all of the structures have been included in Supporting Information. For the rotated structures and the rotated-planar C_{2v} structures, the unique imaginary frequencies associated with each molecule, are given in Table 3. The C_s structures are characterized by one imaginary frequency corresponding to rotation about the A−X bond and the C_{2v} structures by two imaginary frequencies with the second imaginary frequency corresponding to inversion at X. The molecular structures for the optimized ground states and the lowest energy transition states for rotation are shown in Figure 1.

The rotation process leads to breaking the π-bond and a consequent lengthening of the XY bond. The BN bond length of BH_2NH_2 increases by 0.084 Å in going from the planar



BH_2NH_2 Rotated BH_2NH_2

AlH_2NH_2 Rotated AlH_2NH_2

BH_2PH_2 Rotated BH_2PH_2

AlH_2PH_2 Rotated AlH_2PH_2

Figure 1. Optimized molecular structures for BH_2NH_2, AlH_2NH_2, BH_2PH_2, AlH_2PH_2, and the corresponding rotated structures.

TABLE 4: Components for Calculated Atomization Energies[a]

molecule	CBS[b]	ΔE_{ZPE}[c]	ΔE_{CV}[d]	ΔE_{SR}[e]	ΔE_{SO}[f]	ΣD_0(0 K)[g]
BH_2	169.28	8.97	0.72	−0.06	−0.03	160.95
AlH_2	125.53	6.36	−0.91	−0.28	−0.21	117.76
PH_2	154.32	8.32	0.19	−0.22	0.00	145.96
BH_2NH_2(rot)	467.89	27.75	1.55	−0.36	−0.03	441.30
BH_2NH_2(rot-planar)	463.38	27.13	1.59	−0.42	−0.03	437.39
BH_2PH_2(rot)	406.37	22.67	1.28	−0.43	−0.03	384.52
BH_2PH_2(rot-planar)	373.49	22.20	0.97	−0.79	−0.03	351.44
AlH_2NH_2(rot)	411.19	22.85	−0.31	−0.70	−0.21	387.12
AlH_2NH_2(rot-planar)	410.67	22.58	−0.45	−0.73	−0.21	386.70
AlH_2PH_2(rot)	351.94	18.36	−0.59	−0.69	−0.21	332.08
AlH_2PH_2(rot-planar)	330.91	18.10	−0.99	−1.04	−0.21	310.57

[a] In kcal/mol. [b] Extrapolated by using eq 1 with aug-cc-PVnZ, n = D, T, Q. [c] The zero point energies were obtained as described in the text. [d] Core−valence corrections were obtained with the cc-pwCVTZ basis sets at the aVTZ optimized geometries for the transition states for rotation and at the aVDZ optimized geometries for the rotated-planar structures. [e] The scalar relativistic correction is based on a CISD(FC)/cc-pVTZ MVD calculation at the aVTZ optimized geometries for the transition states for rotation and at the aVDZ optimized geometries for the rotated-planar structures. [f] Correction due to the incorrect treatment of the atomic asymptotes as an average of spin multiplets. Values are based on C. Moore's Tables, ref 39. [g] The theoretical value of the dissociation energy to atoms, ΣD_0(0 K).

ground-state configuration to the 90°-rotated C_s symmetry transition state structure. For the rotated-planar C_{2v} structure of BH_2NH_2, the XY bond shows a smaller increase of 0.067 Å. A similar increase was found for BH_2PH_2 with the BP bond lengthening of 0.082 Å from the ground state to the rotated structure. There was a decrease in the XY bond distance of 0.017 Å going from the rotated to the planar-rotated C_{2v} structure. Upon rotation, a smaller increase of 0.040 Å was found for the AlN bond of AlH_2NH_2 from the planar ground state to the C_s transition state structure. In going from the rotated C_s structure to the planar-rotated C_{2v} structure, a similar decrease of 0.018 Å was predicted as was found for the other molecules. The AlP bond of AlH_2PH_2 had a similar small increase of 0.027 Å on rotation to the C_s structure. In going from the rotated C_s structure to the rotated-planar C_{2v} structures, there was a considerable decrease in the AlP bond distance of 0.070 Å. In comparison, Dobbs and Hehre[9] calculated a much larger increase of 0.15 Å in the C−C bond length in going from the planar to the twisted form of ethylene at the UHF/6-31G* level. We note that the rotated form of C_2H_4 is a diradical as compared to the closed shell with a lone pair structure found in rotated AH_2XH_2.

The total valence CCSD(T) energies as a function of basis set are given in Supporting Information. The calculated energy components for the total atomization energies are given in Table 4 and the calculated heats of formation at 0 K and 298 K are given in Table 5. The previously reported results for the ground states are reported for completeness, and the results for planar (C_{2v}) BH_2PH_2 and AlH_2PH_2 also are given in Table 5.[3,4] The relativistic corrections for the structures investigated are all negative and reasonably small ranging from −0.06 to −1.04 kcal/mol. The core-valence corrections are positive for the BH_2, PH_2, BH_2NH_2, and BH_2PH_2 and range from 0.2 to 1.6 kcal/mol. For AlH_2, AlH_2NH_2, and AlH_2PH_2, the core valence corrections are negative and range from −0.3 to −1.0 kcal/mol.

The π-bond energies can be estimated from the magnitude of the energies of the rotation barriers. There are three values for the rotation barrier given in Table 6. The adiabatic rotation energy barriers were calculated as the energy difference between the equilibrium ground-state configuration and the C_s transition state for torsion about the A−X bond. The values from the C_s or C_{2v} ground state to the rotated C_{2v} structure were calculated as were the values for the rotation barrier from a C_{2v} planar structure to a C_{2v} rotated structure.

The adiabatic rotation barrier of borane amine is 29.9 kcal/mol, which is much larger than found for the other molecules and indicative of a strong dative π-bond between B and N. This value is much lower than the π-bond strength of 65 kcal/mol^{-1} in ethylene[11]obtained from the rate of cis−trans isomerization in 1,2-dideuterioethylene. Our value for BH_2NH_2 is in good agreement with that of Allen and Fink,[12] who predicted a rotational barrier (C_s symmetry transition state) of 32.4 kcal/mol at the CISD+Q/DZ+P level and of McKee[14] who predicted 32.1 kcal/mol at the MP4/6-31+G(2d,p) level of theory.

TABLE 5: Calculated Heats of Formation (kcal/mol) at 0 K and 298 K

molecule	$\Delta H_f(0\ K)_{theory}$	$\Delta H_f(298\ K)_{theory}$
BH_2	78.5	78.6
AlH_2	63.7	63.0
PH_2	32.7	31.8
BH_2NH_2 (rot)	14.0	11.1
BH_2NH_2 (rot-planar)	17.9	15.0
BH_2PH_2 (rot)	33.6	30.7
BH_2PH_2 (rot-planar)	66.7	63.8
AlH_2NH_2 (rot)	10.2	7.1
AlH_2NH_2 (rot-planar)	10.6	7.2
AlH_2PH_2 (rot)	28.1	24.8
AlH_2PH_2 (rot-planar)	49.6	46.2
BH_2NH_2 (GS C_{2v})[a]	−15.9	−18.6
AlH_2NH_2 (GS C_{2v})[b]	−0.3	−3.3
BH_2PH_2 (GS C_s)[b]	24.4	21.8
BH_2PH_2 (planar C_{2v})[b]	31.0	28.2
AlH_2PH_2 (GS C_s)[b]	25.4	22.6
AlH_2PH_2 (planar C_{2v})[b]	35.4	32.2

[a] Ref 3. [b] Ref 4.

The adiabatic dative π-bond energy of H_2AlNH_2 is about one-third that of borane amine, 10.5 kcal/mol, consistent with the smaller change in bond distance on rotation and the lower π-bond energy expected for a bond between a 1st and 2nd row metal. The lower level values calculated by Fink[19] and Davy[20] of 11.2 and 11.0 kcal/mol, respectively, are in excellent agreement with our higher level calculation. Borylphosphine, H_2BPH_2, has a similar adiabatic π-bond energy of 9.2 kcal/mol. Surprisingly, the B−P bond distance increases by an amount comparable to that of BH_2NH_2 on rotation even though the latter has a much higher barrier. Borden[18] calculated the adiabatic barrier to rotation in BH_2PH_2 to be 10.4 kcal/mol at the MP4 level of theory, which is in good agreement with our value. Allen et al.[16] also calculated the rotational barrier in BH_2PH_2 through a transition state of C_s symmetry at 10.0 kcal/mol. The rotational energy barrier for the phosphine alane was considerably smaller than the others indicating a very weak adiabatic π-bond between AlP. The adiabatic π-bond energy

TABLE 6: Rotation Barriers (π-Bond Energies) and Inversion Barriers at N or P[a]

molecule	rotation (G.S $\rightarrow C_s$) adiabatic[b]	rotation ($C_s \rightarrow C_{2v}$)	rotation ($C_{2v} \rightarrow C_{2v}$) inherent[c]	inversion (ground state)	inversion (rotated)
$H_2B{=}NH_2$	29.9	33.8	33.8	0[d]	3.9
$H_2Al{=}NH_2$	10.5	10.9	10.9	0[d]	0.4
$H_2B{=}PH_2$	9.2	42.3	35.7	6.6	33.1
$H_2Al{=}PH_2$	2.7	24.2	14.2	10.0	21.5

[a] In kcal/mol. [b] Adiabtic π-bond energy. [c] Intrinsic π-bond energy. [d] Planar ground-state structure.

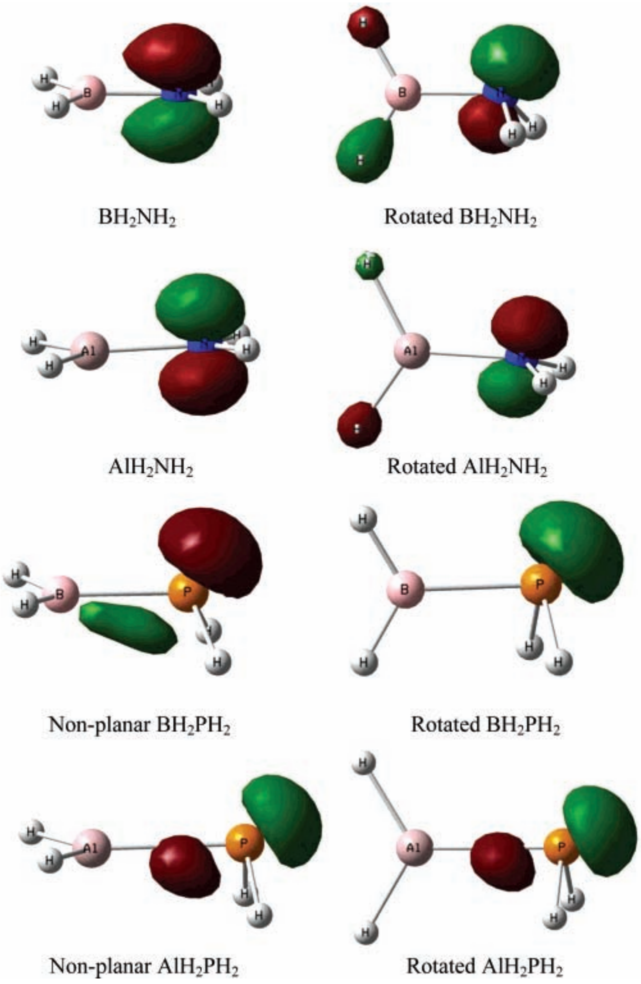


Figure 2. HOMO for the ground state and rotated structures of BH_2-NH_2, AlH_2NH_2, BH_2PH_2, and AlH_2PH_2.

of H_2AlPH_2 was about one-third that of borane phosphine's at 2.7 kcal/mol.

We provide plots of the highest occupied molecular orbital (HOMO) at the Hartree−Fock level for the ground state and the transition state for rotation in Figure 2. The HOMO in the planar structures corresponds essentially to a lone pair on N or P that can delocalize to the B or Al. The largest delocalization is found for BH_2NH_2 as expected from this compound having the highest barrier. The other molecules, which have much lower rotation barriers, show less delocalization from the lone pair on X toward the empty orbital on A with the smallest change in the orbitals found for AlH_2PH_2, the compound with the lowest barrier. There is a small interaction of the lone pair on N with the A−H orbitals in the rotated transition state. The orbital plots confirm that the π-bond in these AH_2XH_2 compounds is best described as a dative bond just as found for the σ-bond in the AH_3XH_3 compounds.

We also calculated a rotation barrier as the energy difference between the ground state and the rotated-planar C_{2v} structures. This information can be used to provide insights into the heights of the barriers. The rotation barrier for BH_2NH_2 is 33.8 kcal/mol going from the C_{2v} ground state to the rotated C_{2v} structure, similar to the value of 37.9 kcal/mol of Allen and Fink.[12] A much smaller value of 10.9 kcal/mol was obtained for the C_{2v}-C_{2v} rotational barrier in AlH_2NH_2. The barrier to rotation in going from the ground-state nonplanar BH_2PH_2 C_s structure to the rotated C_{2v} structure is 42.3 kcal/mol, similar to the values obtained by Borden[18] of 44.6 kcal/mol and by Allen and Fink[16] of 46.4 kcal/mol. In AlH_2PH_2, the C_s-C_{2v} rotation barrier is 24.2 kcal/mol. The final rotation barrier to be considered is the barrier to rotation between the planar C_{2v} structure and the rotated-planar C_{2v} structure for BH_2PH_2 and AlH_2PH_2 with respective values of 35.7 and 14.2 kcal/mole.

To better understand the rotation energies, we need to consider the inversion barriers at N and P. The molecular structures of most BY_3 and AlY_3 compounds are planar so inversion does not occur at them. We calculate a barrier height for the inversion of ammonia of 5.1 kcal/mol at the CCSD(T)/CBS limit, about 0.7 kcal/mol below the experimental[13] barrier height of 2020 ± 12 cm^{-1} (5.77 kcal/mol). Including the zero-point contribution, we obtain a value of 5.0 kcal/mol for the inversion of NH_3. We calculate the inversion barrier of PH_3 to be 33.6 kcal/mol that decreases to 32.9 kcal/mol with the zero-point correction included. This value is similar to that of Marynick and Dixon[17] who calculated a barrier for PH_3 of 34.4 kcal/mol at the SCF−CI/DZ+P level including an estimate for quadruple excitations.

We calculated the inversion of the nonplanar $-PH_2$ moiety in the ground-state structures of BH_2PH_2 and AlH_2PH_2 to be 6.6 and 10.0 kcal/mol, respectively, with both considerably less than the inversion barrier of PH_3. This is consistent with the fact that the BH_2 and AlH_2 groups are electropositive, which is known to decrease the inversion barrier. In addition, the presence of the dative π-bond can lower the inversion barrier. Borden[18] finds a smaller barrier to planarity in BH_2PH_2 of 4.5 kcal/mol at the MP4/6-31G* level.

The barriers to inversion of the $-NH_2$ and $-PH_2$ moieties in the rotated structures at the CCSD(T)/CBS level also were calculated. This provides an estimate of the electropositive effect as no π-bond is present. For BH_2NH_2, the barrier to invert NH_2 in the rotated structure is 3.9 kcal/mol, slightly lower than our calculated value of 5.0 kcal/mol for the inversion barrier of NH_3, showing a small effect of substitution of BH_2 for H when there is no overlap of the lone pair on N with the vacant orbital on B. For rotated AlH_2NH_2, the barrier to inversion was 0.4 kcal/mol considerably less than that in BH_2NH_2, and consistent with the fact that AlH_2 is more electropositive than BH_2. For rotated BH_2PH_2, the barrier to inversion of the $-PH_2$ moiety was 33.1 kcal/mol showing essentially no effect of substituting BH_2 for H, just as was found for the nitrogen analogue. For rotated AlH_2-PH_2, the barrier to inversion was 21.5 kcal/mol, considerably less than that in BH_2PH_2. The decrease of 11.4 kcal/mol on substitution of AlH_2 for H is again consistent with AlH_2 being more electropositive than BH_2 or H.

TABLE 7: Adiabatic ($\sigma + \pi$) Total Dissociation Energies[a]

molecule	adiabatic total dissociation energy	adiabatic σ-bond energy
$H_2B{=}NH_2$	139.7	109.8
$H_2Al{=}NH_2$	109.3	98.8
$H_2B{=}PH_2$	86.8	77.6
$H_2Al{=}PH_2$	71.0	68.3

[a] In kcal/mol.

On the basis of these values, we can now reexamine the π-bond strengths. For BH_2NH_2 and AlH_2NH_2, the differences between the rotation barrier proceeding through the rotated C_s and C_{2v} structures are similar due to the relatively small inversion barrier at N. For BH_2PH_2 and AlH_2PH_2, the difference between the rotation barrier proceeding through the rotated C_s and C_{2v} structures is due to the much larger inversion barrier at P. The tendency for the phosphorus atom to pyramidalize serves to weaken the π-bond energy because there is reduced overlap between the lone pair on P and the vacant orbital at B or Al. We can estimate this effect by comparing the inversion barriers in the unrotated and rotated states which corresponds to the C_{2v}-C_{2v} energy difference. For BH_2PH_2, this value is 35.7 kcal/mol and, in AlH_2PH_2, this value is 14.2 kcal/mol.

The adiabatic π-bond energies are the ground state (GS) to C_s values given in Table 6. The intrinsic π-bond energies are given by the adiabatic bond energy plus the energy used to invert the N or P atom or the $C_{2v} \rightarrow C_{2v}$ rotation energies. The intrinsic B=N π-bond energy is thus 34 kcal/mol and the intrinsic Al=N π-bond energy is 11 kcal/mol, both similar to the adiabatic values. The intrinsic B=P π-bond energy is 36 kcal/mol and the intrinsic Al=P π-bond energy is 14 kcal/mol. The intrinsic π-bond energies for the latter two are substantially different from the adiabatic values because of the high inversion barrier at P. Comparing the intrinsic values, we see that the B=N and B=P values are quite similar and that the Al=N and Al=P values also are similar and substantially smaller.

On the basis of the calculated heats of formations given in Table 5, the adiabatic dissociation energies which correspond to the sum of the σ- and π-bond energies are given in Table 7. The adiabatic reaction energies show that BH_2NH_2 has the largest binding energy at 139.7 kcal/mol, which can be compared with the C−C bond dissociation energy of 171.0 kcal/mol in ethylene.[6] AlH_2NH_2 has a binding energy approximately 20 kcal/mol lower than that of BH_2NH_2 (109.3 kcal/mol). Both the BH_2PH_2 and AlH_2PH_2 have lower binding energies of 86.8 and 71.0 kcal/mol, respectively.

The adiabatic σ-bond energies of the molecules can be calculated as the difference between the binding energy of the optimized ground-state structure, representing the σ-bond + π-bond energies, and the corresponding adiabatic rotational energy barrier, representing the π-bond energy. The adiabatic σ-bond strengths for the molecules BH_2NH_2, AlH_2NH_2, BH_2PH_2, and AlH_2PH_2 from the ($\sigma + \pi$) adiabatic asymptote using the adiabatic rotation barriers are 109.8, 98.8, 77.6, and 68.3 kcal/mol, respectively. The adiabatic σ-bond strength for BH_2NH_2 is comparable to the adiabatic σ-bond strength in ethylene of 106 kcal/mol given the experimentally determined π-bond strength of 65 kcal/mol[11] and an adiabatic C=C bond dissociation energy of 171 kcal/mol.[5] The fact that it is slightly higher is consistent with the fact that the bond in BH_2NH_2 includes some ionic character. If we use the intrinsic π-bond strengths, we lower the adiabatic σ-bond strength to 106 kcal/mol for BH_2NH_2. For AlH_2NH_2, use of the intrinsic π-bond strength results in very little change, a σ-bond strength of 98 kcal/mol. For BH_2PH_2 and AlH_2PH_2, use of the intrinsic π-bond strengths leads to substantially lower σ-bond strengths of 51.1 and 56.8 kcal/mol, respectively.

The adiabatic σ-bond energies can be compared to the bond dissociation energies of the diatomics BN, AlN, BP, and AlP that are 102.4, 57.3, 76.4, and 50.9 kcal/mol at 0 K, respectively.[3,4] Thus the σ-bond energies are stronger in the molecular systems than in the diatomics. In contrast, the dissociation energy[41] of C_2 is 148 kcal/mol, much higher than the C−C σ-bond energies in most organic compounds.

The σ-bond energies for the AH_2XH_2 compounds can be compared to the dative σ-bond energies in the corresponding AH_3XH_3 compound (Table 1). The σ-bond energies for the AH_2XH_2 compounds are substantially higher than the dative σ-bond energies. As a consequence, the reaction $AH_3XH_3 \rightarrow AH_2XH_2 + H_2$ becomes closer to thermoneutral than in the hydrocarbon case for $CH_3CH_3 \rightarrow CH_2CH_2 + H_2$, which is substantially endothermic. Only for the BH_3PH_3 reaction is a substantial endothermicity found, and this is consistent with the relatively low σ-bond energy.

Carter and Goddard[8] have shown that most of the decrease in the dissociation energy of C_2F_4 to $2CF_2$ as compared to the dissociation energy of C_2H_4 to $2CH_2$ is due to the difference in the ground states of CF_2 and CH_2. The singlet ground state of CF_2 is not optimal for forming the σ- and π-bonds in C_2F_4, so the total dissociation energy is substantially reduced by the promotion energy to the triplet configuration, which is optimal for forming C_2F_4. In C_2H_4, the triplet ground state of CH_2 is optimal for forming C_2H_4, so there is no reduction in the total bond dissociation energy. Borden[7] has suggested that the same types of arguments need to be considered in comparing the strengths of the π-bonds in C_2H_4 and HCCH. This is because the optimal state of CH for forming HCCH is the $^4\Sigma^-$, which is 16.7 kcal/mol above the $^2\Pi$ ground state.

This approach can be applied to analyze the bonding of AH_2XH_2 compounds to derive an intrinsic total ($\sigma + \pi$) bond dissociation energy. The bonding in the molecules at equilibrium corresponds to BH_2 or AlH_2 in the ground state and the NH_2 or PH_2 in the excited state. The excited state for XH_2 is the $^2A_1$ with the unpaired electron in the plane and the lone pair orbital out of the plane. For NH_2, T_0 ($^2B_1 \rightarrow {}^2A_1$) is 31.8 kcal/mol and for PH_2, T_0 is 52.2 kcal/mol.[42] To a first approximation, the bonding in $H_2A = XH_2$ can be described as arising from the $^2A_1$ configurations of both fragments. Thus, the sum of the bond energies in the diabatic limit or the intrinsic total ($\sigma + \pi$) bond dissociation energy would be increased by 31.8 kcal/mol for BH_2NH_2 and AlH_2NH_2 and by 52.2 kcal/mol for BH_2PH_2 and AlH_2PH_2 giving respective values of 171.5, 141.1, 139.0, and 123.2 kcal/mol. If the intrinsic total ($\sigma + \pi$) bond dissociation energy is used, then BH_2NH_2 has a σ-bond strength of 142 kcal/mol using the adiabatic rotation barrier and one of 138 kcal/mol using the intrinsic π-bond energy. For AlH_2NH_2, the σ-bond strengths are 131 and 130 kcal/mol, respectively, using the two definitions of the π-bond energy. For BH_2PH_2, the σ-bond energies would be 130 kcal/mol with the adiabatic π-bond energy and 103 kcal/mol with the intrinsic the π-bond energy. For AlH_2PH_2, the σ-bond energies would be 121 kcal/mol with the adiabatic π-bond energy and 109 kcal/mol with the intrinsic π-bond energy. These values seem to be somewhat high and are not consistent with other chemical concepts.

This analysis suggested another way to analyze the bonding in these molecules. Because the π-bond is best described as a dative bond (see Figure 2), it is appropriate to compare breaking the σ-bond in these compounds to breaking an AH_2−R or XH_2−R bond. The simplest comparison is to consider R as H and compare the A−H and X−H bond energies to the A−X bond energies. Feller et al.[43] calculated the heats of formation of some simple boron compounds and predicted $\Delta H_f^0(BH_2, 0\ K) = 78.4$ kcal/mol and $\Delta H_f^0(BH, 0\ K) = 106.2$ kcal/mol at the CCSD(T)/CBS level. These values for BH_2 and BH are in good agreement with our current value of 78.5 and 106.2 kcal/mol, respectively, where we have included scalar-relativistic and spin−orbit corrections, which were not included previously. Given the heat of formation of BH_3 of 26.4 kcal/mol at 0 K,[3] we calculate a B−H bond energy of 103.7 kcal/mol (see Table 8). In the present study, we have calculated the heats for formation at 0 K of the triatomics AlH_2 and PH_2, giving values of 63.7 and 32.7 kcal/mol, respectively, and the corresponding diatomics AlH and PH, giving values of 58.9 and 57.0 kcal/mol, respectively. Given $\Delta H_f^0(AlH_3, 0\ K) = 31.9$ kcal/mol and $\Delta H_f^0(PH_3, 0\ K) = 3.3$ kcal/mol,[4] the resulting Al−H bond energy in AlH_3 is 83.4 kcal/mol, while the P−H bond energy in PH_3 is 81.0 kcal/mol. These can be compared to the B−H bond energy of 103.7 kcal/mol in BH_3 and the N−H bond energy of 106.5 kcal/mol in NH_3.[3] The bond energies for HAl−H and HP−H in going to the corresponding diatomic species are 46.8 kcal/mol at 0 K and 75.9 kcal/mol at 0 K, respectively, and can be compared to the value of the H−BH bond energy of 79.3 kcal/mol and the H−NH bond energy of 92.3 kcal/mol at 0 K.[21m]

Comparison of the AH_3 and XH_3 bond energies in Table 8 with the A−B adiabatic σ-bond energies in Table 7 shows that the X−H bond energies track the A−B bond energies. The σ-bond energy in BH_2NH_2 is larger than the N−H bond energy in NH_3 by only 3 kcal/mol. The σ-bond energy in AlH_2NH_2 is less than that in BH_2NH_2 by 11 kcal/mol as is expected as Al is a 2nd row atom and the bond energy is only 8 kcal/mol less than the N−H bond energy in NH_3. For $BH_2{=}PH_2$ and $AlH_2{=}PH_2$, the σ-bond energies are 3 and 13 kcal/mol, respectively, less than the P−H bond energy in PH_3, which is essentially the same trend found in comparing the σ-bond energies in $BH_2{=}NH_2$ and $AlH_2{=}NH_2$ with the N−H bond energy in NH_3. Thus, the σ-bond energies resemble very closely the XH_3 bond energies, and it is not appropriate to compare with the diabatic limit approximation given above. The bonding in these compounds is much closer to that in a normal NH_2R or PH_2R compound with a delocalized lone pair (dative π-bond) from N or P as compared to a model that describes the bonding as a fully shared π-bond as found in C_2H_4. This result is consistent with Pauling's electroneutrality rule[44] as one would have to write the structure of BH_2NH_2 as $^-H_2B{=}NH_2^+$ with formal charges that puts the negative charge on the least electronegative atom B and the positive charge on the more electronegative atom N, which is the reverse of where the charges want to be.

The bond energies for the H_2AXH_2 compounds provide us with some useful insights into the differences in the donor−acceptor chemistry and covalent bond carbon-based chemistry. The elimination reaction 4 for loss of H_2 from BH_3NH_3 in the gas phase is exothermic

$$BH_3NH_3 \rightarrow BH_2NH_2 + H_2 \qquad \Delta H(298\ K) = -5.1\ \text{kcal/mol} \quad (4)$$

whereas the comparable organic reaction 5 is substantially endothermic.[3]

$$C_2H_6 \rightarrow C_2H_4 + H_2 \qquad \Delta H(298\ K) = 32.6\ \text{kcal/mol} \quad (5)$$

This difference in energetic requirements for H_2 release is because a weak B−N dative σ-bond is broken in BH_3NH_3 and a strong sp^2-sp^2 σ-bond is formed in BH_2NH_2, whereas a strong σ-bond is broken in C_2H_6 and a σ-bond of comparable strength to that in BH_2NH_2 is formed in C_2H_4. Even though the adiabatic π-bond energy of BH_2NH_2 is only 30 kcal/mol as compared to the value of 65 kcal/mol in C_2H_4, the difference of 35 kcal/mol is much smaller than the difference of 63 kcal/mol for the σ-bond strengths in BH_3NH_3 and C_2H_6. Thus, the difference in the reactant σ-bond strengths is more important than the differences in the product π-bond strengths, because the strength of the σ-bonds in the product are comparable. The differences in the σ- and π-bond strengths also can be observed in the bond distances. The change in the C−C bond length[45] from C_2H_6 to C_2H_4 is 0.20 Å, whereas the difference in the B−N bond lengths between BH_3NH_3 and BH_2NH_2 is 0.26 Å. The larger difference in the latter pair is consistent with the larger change in the σ-bond strengths in the boron amines, even though the π-bond strength is lower in the boron amines. The π-bond shortens the B−N bond length by 0.08 Å obtained by comparing the ground state and rotated structures for BH_2NH_2. In C_2H_4, the difference has been calculated[9] to be 0.15 Å at the UHF/6-31G* level (C_2H_4 vs twisted $\cdot CH_2CH_2 \cdot$), a larger difference consistent with the stronger π-bond in C_2H_4. The value of 1.465 Å for the diradical sp^2-sp^2 σ-bond is consistent with the experimental[46] and calculated[47] values of 1.45 to 1.47 Å for the C−C sp^2-sp^2 σ-bond in s-*trans*-1,3-butadiene.

TABLE 8: AH_2-H and XH_2-H σ Bond Energies[a]

molecule	adiabatic σ-bond energy
BH_3	103.7
NH_3	106.5
AlH_3	83.4
PH_3	81.0

[a] In kcal/mol.

Conclusions

Ab initio molecular orbital theory at the CCSD(T)/CBS level plus additional corrections have been used to predict the σ- and π-bond energies of BH_2NH_2, AlH_2NH_2, BH_2PH_2, and AlH_2PH_2. The adiabatic π-bond energy was defined as the barrier to rotation between the ground state and C_s transition state structures, and the intrinsic π-bond energy was defined as the adiabtiac π-bond energy corrected for inversion at N or P. Using the adiabatic dissociation energies for AH_2XH_2 to $AH_2 + XH_2$, the adiabatic σ- and π-bond energies, respectively, for BH_2NH_2 are 109.8 and 29.9 kcal/mol; for AlH_2NH_2 , 98.8 and 10.5 kcal/mol; for BH_2PH_2, 77.6 and 9.2 kcal/mol; and for AlH_2PH_2, 68.3 and 2.7 kcal/mol. These results are consistent with the binding being best described as breaking a σ-bond in an NH_2R or PH_2R molecule that contains a delocalized lone pair (a dative π-bond). The energy differences between the weak dative σ-bond energies in AH_3XH_3 compounds and the strong sp^2-sp^2 σ-bonds in the AH_2XH_2 compounds are an important reason why H_2 can readily be released from AH_3XH_3 compounds (except for BH_3PH_3) in contrast to C_2H_6 where loss of H_2 is substantially endothermic.

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Supporting Information Available: Optimized CCSD(T) geometry parameters for AH_2, XH_2, and planar NH_3 and PH_3, calculated vibrational frequencies, and total CCSD(T) energies (E_h) as a function of basis set extrapolated to the complete basis set limit. This material is available free of charge via the Internet at http://pubs.acs.org.

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