# G2(MP2) Molecular Orbital Study of $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and $H_3AlYH_3$ (Y = N, P, and As) Complexes

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$[H_3AlXH_3]^-$ (X = C, Si, and Ge) and $H_3AlYH_3$ (Y = N, P, and As) have been investigated as donor−acceptor complex types at the G2(MP2) level of theory. Both staggered and eclipsed conformations have been examined. For all complexes, the first one is found to be favored. The G2(MP2) results show that the anionic complexes are more stable than the neutral ones. They show also that this stability decreases when going from carbon to germanium for $[H_3AlXH_3]^-$ complexes and from nitrogen to arsenic for $H_3AlYH_3$ complexes. The interaction diagrams prove that the evolution of complexation energy depends on the coordination mode. In fact, this is a simple "HOMO−LUMO" interaction for $[H_3AlXH_3]^-$ anionic complexes, while for the $H_3AlYH_3$ neutral ones it is a result of two interaction types: interaction between "$a_1$" symmetry fragments orbital (stabilizing) and interactions between "e" symmetry fragments orbital (destabilizing). A linear relationship has been established and discussed between the G2(MP2) complexation energy and the ligand G2(MP2) proton affinity, whereas no correlation has been found with the charge transfer.

## 1. Introduction

Lewis acids have long been known as catalysts in organic reactions. The types of reactions in which trivalent aluminum plays a catalytic role are many and varied. The Friedel−Crafts alkylation and acylation of aromatic rings, removal of *tert*-butyl groups from phenols, and the well-known Ziegler−Natta polymerization reactions are some examples in which the aluminum trichloride acts as catalyst. Many of these important compounds have been experimentally and theoretically studied extensively.[1−10] Recently, Andrews et al.[1] have published an interesting work concerning the reaction of laser-evaporated aluminum atom with molecular fluorine, chlorine, bromine, and iodine leading to mono-, di-, and trihalide aluminum. Vibrational spectroscopy and computational geometries of these aluminum halides are well-known. The complexing behavior of Aluminum trihalide ($AlX_3$) has also been the subject of many experimental and theoretical works.[11−29] The points that have been more developed are conformational structure, complexation energy, and charge transfer. In fact, Jasien[11] investigated computationally on a series of $AlX_3$−R (R = $H_2CO$, HClCO, $C_2H_4$, $C_2H_2$, and $H_3CCl$) compounds, searching, unsuccessfully, a correlation between the binding energy and the charge transfer. LePage and Wiberg[12] have examined the energy and conformational barriers in $AlCl_3$−formaldehyd ($H_2CO$) complex. In the same perspective, Cannolly and Dudis[13] studied $AlCl_3$ complexes with $NH_3$ and $H_2S$.

Previous high-quality ab initio computational studies of the Lewis acid chemistry of $AlX_3$ complexes have generally dealt with the chemistry of the aluminum trihydride ($AlH_3$). This latter, as well as $GaH_3$, plays an important role in a wide range of chemical process. Aluminum hydride is used in photography and photoimaging and has recently been implicated in hydrogen desorption from aluminum crystal.[17] It has been shown that their derivatives can be used in a new approach toward AlN/BN materials.[18] The presence of M−H rather than M−C bonds in these compounds reduces the degree of carbonaceous contaminant in deposited material, which can ensure greater reproducibility and more consistent electronic properties. In addition, more studies that have dealt directly with the complex question of reactivity in complexes of $AlH_3$ are those of Sakai.[19,20] In these studies, the primary steps in a Ziegler−Natta polymerization reaction for both acetylene ($C_2H_2$) and ethylene ($C_2H_4$) were modeled using a metathesis-type mechanism. Bates and Dwyer [21] used an $AlH_3$ fragment in their model of CO adsorption in zeolites; their conclusion was that the "Lewis site model" for adsorption of CO was energetically favorable and more consistent with experimental work.

Many theoretical works have been realized regarding the $H_3AlNH_3$ compound. Edwards and Jones[22] determined the geometry of the $H_3AlNH_3$ complex at the self-consistent field level of theory and with various basis sets. The purpose of their work was to study basis set effects, which were then applied to the $(CH_3)_3GaYH_3$ (where Y = N, P, and As) complexes. Chey et al.[23] optimized the equilibrium structure of $H_3AlNH_3$ using Hartree−Fock and second-order Möller−Plesset perturbation (MP2) methods in conjunction with basis sets of up to 6-31G(d) quality for comparison to $\pi$ complexes of trivalent aluminum compounds with alkenes. Atwood et al.[24] also report predicted geometries of $H_3AlNH_3$, determined at the HF level using a double-$\zeta$ plus polarization (DZP) basis set. Their work was done to study the energy of dimerization of trimethylamine alane (TMAA) $H_3AlN(CH_3)_3$. Marsh et al.[25] have reported the dissociation energy of $H_3AlNH_3$. They presented theoretical predictions of the vibrational spectra of amonia alane so that experimental detection and characterization of $H_3AlNH_3$ may be facilitated. They showed that the nature of the Al−N bond in the simple donor−acceptor analogue, ammonia alane ($H_3AlNH_3$), should give insight into the bonding in the larger TMAA molecule. Haaland[26] suggests that the dissociation energy of TMAA should be similar to the 30 kcal/mol dissociation energy of trimethylamine trimethylalane.

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**TABLE 1: MP2(full)/6-31G(d) Bond Length (Å) and Bond Angle (deg)**

| compound | Al−X | Al−H | X−H | ∠H−Al−X | ∠H−Al−H | ∠H−X−Al or ∠H−X−$C_3$ axis | ∠H−X−H |
|---|---|---|---|---|---|---|---|
| $AlH_3$ |  | 1.589 |  | 90. | 120. |  |  |
| $[CH_3]^-$ |  |  | 1.121 |  |  | 116.5 | 101.6 |
| $[SiH_3]^-$ |  |  | 1.542 |  |  | 121.8 | 94.8 |
| $[GeH_3]^-$ |  |  | 1.621 |  |  | 123.0 | 93.2 |
| $[H_3AlCH_3]^-$ | 2.030 | 1.655 | 1.098 | 110.0 | 109.0 | 112.2 | 106.7 |
| $[H_3AlSiH_3]^-$ | 2.511 | 1.638 | 1.510 | 107.8 | 111.0 | 116.5 | 101.6 |
| $[H_3AlGeH_3]^-$ | 2.510 | 1.635 | 1.583 | 107.3 | 111.5 | 117.2 | 100.7 |
| $NH_3$ |  |  | 1.017 |  |  | 112.4 | 112.4 |
| $PH_3$ |  |  | 1.415 |  |  | 121.9 | 94.6 |
| $AsH_3$ |  |  | 1.536 |  |  | 124.0 | 91.8 |
| $H_3AlNH_3$ | 2.083 | 1.606 | 1.020 | 99.44 | 117.4 | 111.4 | 107.5 |
| $H_3AlPH_3$ | 2.546 | 1.601 | 1.405 | 97.27 | 118.4 | 118.5 | 99.2 |
| $H_3AlAsH_3$ | 2.593 | 1.600 | 1.524 | 97.26 | 118.4 | 120.0 | 97.3 |

**TABLE 2: G2(MP2) Total Energies ($E_{tot}$ in au) of Complexes and Difference Energy Δ*E* (kcal/mol)**

| complex | $E_{tot}$ staggered | $E_{tot}$ eclipsed | $\Delta E^a$ |
|---|---|---|---|
| $[H_3AlCH_3]^-$ | −283.63199 | −283.63049 | 0.942 |
| $[H_3AlSi\ H_3]^-$ | −534.65932 | −534.65793 | 0.872 |
| $[H_3AlGe\ H_3]^-$ | −2321.05162 | −2321.05053 | 0.684 |
| $H_3AlN\ H_3$ | −300.24899 | −300.24835 | 0.402 |
| $H_3AlP\ H_3$ | −586.44590 | −586.44458 | 0.828 |
| $H_3AlAs\ H_3$ | −2479.84298 | −2479.84202 | 0.602 |

[a] Difference energy between the eclipsed and the staggered conformation.

Our group has recently published interesting theoretical works on the boron donor−acceptor complexes.[30−34] The computational structural results were in good agreement with the experimental data. We have reported that the complex stability is linearly correlated to proton affinity of the donor ligand. Moreover, we have shown that the complexation energy is correlated to the $^{11}$B NMR coupling constant $^1J_{B-H}$.[30] Also, we have discussed the attractor and donor substituant effect on the structural geometry, complexation energy, and charge transfer. In this paper, we have investigated the anionic alane compounds $[H_3AlXH_3]^-$ (X = C, Si, and Ge) compared to the isoelectronic neutral $H_3AlYH_3$ (Y = N, P, and As) ones. The relative stabilities of these complexes are examined with respect to the qualitative molecular orbital analysis (QMOA).[35,36] The QMOA arguments have proven useful and successful for predicting the broad outlines of calculations.[30,35,36] They enhance understanding of the relationship between the approximate orbitals we visualize and the detailed results produced by the ab initio calculations. We have showed that, in the case of boron compounds, the interaction donor−acceptor was not based on a simple mixture HOMO−LUMO, but made the seat of an interaction to three orbitals where the $a_1$ occupied orbital of the acceptor fragment cheek a significant role.[30] We will show that, for the alane neutral complexes, a second molecular orbital of donor can be taken into account to explain the evolution of complexation energy in the corresponding column of periodic table. Moreover, we will discus the "e" orbital interaction role on this evolution energy. The choice of the complexes investigated was made with the aim to include different types of strongly bound molecules (anionic one) and coordination compounds (neutral one). A linear correlation between the complexation energies of the complexes and the G2(MP2) calculated proton affinity of $[XH_3]^-$ and $YH_3$ is established and discussed. To the best of our knowledge, no comparative study of these complexes has been carried out.

## 2. Computational Details

Ab initio calculations were performed using the GAUSSIAN92 program.[37] The calculations were performed in the Windows environment on a 266-MHz Pentium II PC having 64 MB of RAM and above 2 Go of available disk storage space.

G2(MP2)[38] is a theoretical procedure for the computation of total energies of molecules at their equilibrium geometries. The G2(MP2) procedure uses the 6-311G(d,p) basis set and corrections for several basis set extensions at the MP2 level. Treatment of electron correlation is made through Möller−Plesset perturbation theory and quadratic configuration interaction (QCISD). The final total energies obtained using the G2(MP2) procedure are effectively at the QCISD(T)/6-311+G(3df,2p)//MP2(full)/6-31G(d) level, making certain assumptions about the additivity of correction. The zero-point vibrational energies, ZPE are obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[39] Finally, a small empirical correction, referred to as the higher level correction HLC is applied to account for the error in the calculated energy of the $H_2$ molecule, and it is based on the number of a and b valence electrons.

All molecules (complexes and fragments) have been investigated at the G2(MP2) level of theory, whereas the electronic structures have been done using the natural bond orbital (NBO)[40] partitioning scheme at the MP2(full)/6-31g(d) level.

## 3. Results and Discussion

**3.1. Geometries.** For the first time, we have investigated the two possible structures (staggered and eclipsed conformations) for the complexes $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and $H_3AlYH_3$ (Y = N, P, and As) at the MP2(full)/6-31G(d) level of theory. All complexes have a $C_{3v}$ symmetry. Table 1 lists bond lengths and bond angles ($d_{Al-X}$, $d_{Al-H}$, $d_{X-H}$, ∠H−Al−X, and ∠H−X−Al) for the complexes. The G2(MP2) total energies and the energy differences between the two conformations of all complexes are presented in Table 2. For all compounds, the staggered conformation corresponds to a minimum and the eclipsed one corresponds to a transition state, the imaginary frequency being the torsion mode around the Al−X bond. The energy difference between the two conformations is very small, and gives the ligand rotation barrier (Table 2). In all complexes, the Al−X bond length is moderately longer for the eclipsed conformation (Table 1). For the anionic adducts, the Al−X (X = C, Si, and Ge) bond is close to a covalent bond length. The values for $[H_3AlCH_3]^-$, $[H_3AlSiH_3]^-$, and $[H_3AlGeH_3]^-$ systems are 2.030, 2.511, and 2.510 Å, respectively, close to the sum of the two atomic radii of the Al and X atoms (2.019, 2.421, and 2.471 Å for Al−C, Al−Si, and Al−Ge, respectively).[41] However, for the neutral adducts, the

**TABLE 3: Comparison of Present G2(MP2) Dissociation Energy (in kcal/mol) with Other Accurate Theoretical Calculations for the $H_3ALNH_3$ Complex**

| | $D_e$ | $D_0$[a] | ref |
|---|---|---|---|
| G2(MP2) | | 25.24 | this work |
| G2 | | 25.66 | 29 |
| DZP CISD+Q | 30.3 | 26.60 | 25 |
| DZP CCSD | 30.2 | 26.50 | 25 |
| NL-SCF[b] | 25.7 | 22.30 | 28 |
| QCISD(T)/6-31g(d)//MP2/6-31g(d) | 33.56 | 22.40 | 27 |

[a] $D_0$ values include ZPE correction. [b] Local density approximation with nonlocal corrections to the correlation and exchange potentials.

Al−Y bond lengths are longer than the corresponding sum of the atomic radii. These latter are 1.988, 2.348, and 2.458 Å for Y = N, P, and As, respectively,[41] while the MP2(full)/6-31G(d) optimized bond lengths are 2.082, 2.556, and 2.593 Å for Al−N, Al−P, and Al−As, respectively. Upon complexation, the MP2 Al−H and X−H bond values are slightly longer than isolated fragments. The bond angle ∠H−Al−X pass from 90° in free acceptor $AlH_3$ to the tetrahedral value (~108°) in the anionic compounds (X = C, Si, and Ge). In fact, the optimized values at the MP2(full)/6-31G(d) level are 110, 107.3, and 107.3° for ∠H−Al−C, ∠H−Al−Si, and ∠H−Al−Ge, respectively. For the $H_3AlYH_3$ complexes, the bond angle ∠H−Al−Y (Y = N, P, and As) varies slightly in going from free reactants to complex adduct. The optimized values at the same level are 99.4, 97.3, and 97.3° for $H_3AlNH_3$, $H_3AlPH_3$, and $H_3AlAsH_3$, respectively. We can already conclude that there is no same donor behavior in the two series. Moreover, the Al−X (X = C, Si, and Ge) bonds have a covalent character. This has a consequence for the Al geometrical environment, which passes from $D_{3h}$ (flat) in free $AlH_3$ to $T_d$ (pyramidal) in the complex. Nevertheless, the equivalent Al−Y (Y = N, P, and As) bond does not have such a strong effect on the $AlH_3$ fragment's geometry in the complex. The ∠H−Al−Y bond angle increases only by about 8° in going from isolated $AlH_3$ to $H_3AlYH_3$ complex, while this variation is about 18° in the anionic adducts. If we take into account the two behaviors, the bond length, and the lack of geometry variation of the $AlH_3$ fragment, we can conclude also that the Al−Y (Y = N, P, and As) has no covalent character. This result permits us to conclude that the compounds $H_3AlNH_3$, $H_3AlPH_3$, and $H_3AlAsH_3$ are sum classical donor−acceptor complexes whereas the anionic adducts $[H_3AlCH_3]^-$, $[H_3AlSiH_3]^-$, and $[H_3AlGeH_3]^-$ have a covalent character.

For the bond angles (∠H−X−Al and ∠H−Y−Al) there is no notable deviation between the two compound groups. For the anionic one, the MP2(full)/6-31G(d) optimized values are 112.2°, 116.3°, and 117.2° (Table 1) for $[H_3AlCH_3]^-$, $[H_3AlSiH_3]^-$, and $[H_3AlGeH_3]^-$, respectively, while in the free ligand $[XH_3]^-$, this angle is 116.5°, 121.8°, and 123.0° for $[CH_3]^-$, $[SiH_3]^-$, and $[GeH_3]^-$, respectively. One can see that this bond angle increases by about 5° in going from the isolated $[XH_3]^-$ ligand to the complex adduct. For the $YH_3$ (Y = N, P, and As) case, the MP2(full)/6-31G(d) bond angle values in the complex adducts are 111.3°, 118.5°, and 120.0°, respectively, and in isolated ligands $NH_3$, $PH_3$, and $AsH_3$ are 112.4°, 122.0°, and 124.0°, respectively. In this case, the variation is about 4°. Therefore, there is the same complexation effect on the $[XH_3]^-$ (X = C, Si, and Ge) ligands as well as $YH_3$ (Y = N, P, and As) ones.

**3.2. Complexation Energy.** To compare our results to previous works, we present in Table 3 the G2(MP2) computed dissociation energy of the classical donor−acceptor complex, $H_3AlNH_3$, chosen as model, along with previous high-level theoretical calculations. It can be seen that our G2(MP2) results are in good agreement with all previous calculations and the dissociation energy is close to that crudely estimated for trimethylamine alane TMAA by Haaland (30.7 kcal/mol).[26] This energy is taken as the energy difference between the complex and the dissociation products. In Table 4, we give the G2(MP2) proton affinities of donor fragments $[XH_3]^-$ (X = C, Si, and Ge) and $YH_3$ (Y = N, P, and As) which are taken, as in previous works,[30−34] as a quantitative measure of the charge transferred from the ligand to the alane, the G2(MP2) complexation energies of complexes, and NBO-MP2/6-31G(d) charge transfer.

**TABLE 4: Proton Affinities (PA in kcal/mol) of Ligands (L = $[XH_3]^-$ and $YH_3$), G2(MP2) Complexation Energies ($E_{comp}$ in kcal/mol) of Ligands with $AlH_3$ and Charge Transfer Qc(electron)**

| complex | PA[a] | $E_{comp}$[b] | Qc |
|---|---|---|---|
| $[H_3AlCH_3]^-$ | 416.80 | −84.68 | 0.338 |
| $[H_3AlSiH_3]^-$ | 373.10 | −54.42 | 0.577 |
| $[H_3AlGeH_3]^-$ | 361.72 | −49.88 | 0.536 |
| $H_3AlNH_3$ | 202.50 | −25.24 | 0.132 |
| $H_3AlPH_3$ | 186.80 | −12.60 | 0.237 |
| $H_3AlAsH_3$ | 180.80 | −9.75 | 0.239 |

[a] $PA(L) = -[E(LH^+) - E(L)]$. [b] $E_{comp} = E(H_3AlL) - [E(H_3Al) + E(L)]$ with $L = [XH_3]^-$ (X = C, Si, and Ge) and $L = YH_3$ (Y = N, P, and As).

G2(MP2) results show that the anionic $[H_3AlXH_3]^-$ (X = C, Si, and Ge) complexes are more stable than the neutral $H_3AlYH_3$ (Y = N, P, and As) ones. However, the complexation energy decreases for each group in going from C (N, respectively) to Ge (As, respectively). In addition, the complexation energy decreases along a periodic table column with the atomic number. Therefore, the anionic donor−acceptor complexes show rather strong donor−acceptor bonds compared to the neutral adducts. These values can be explained since $[H_3AlCH_3]^-$, $[H_3AlSiH_3]^-$, and $[H_3AlGeH_3]^-$ are isoelectronic to the corresponding stable organic compounds $H_3CCH_3$, $H_3CSiH_3$, and $H_3CGeH_3$, respec-

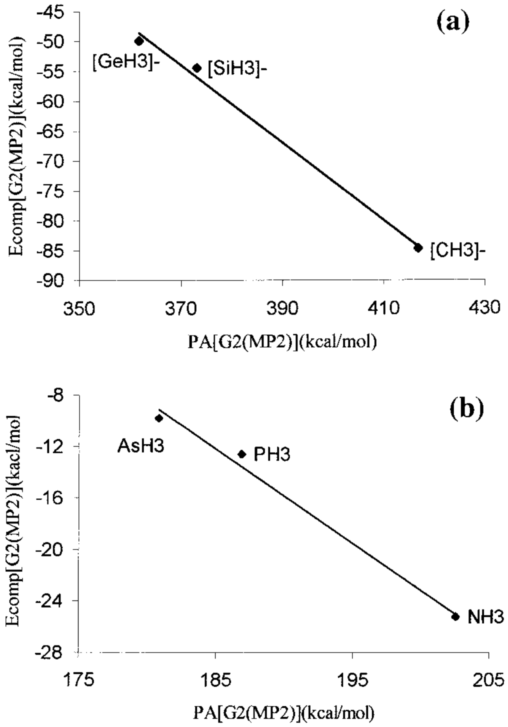
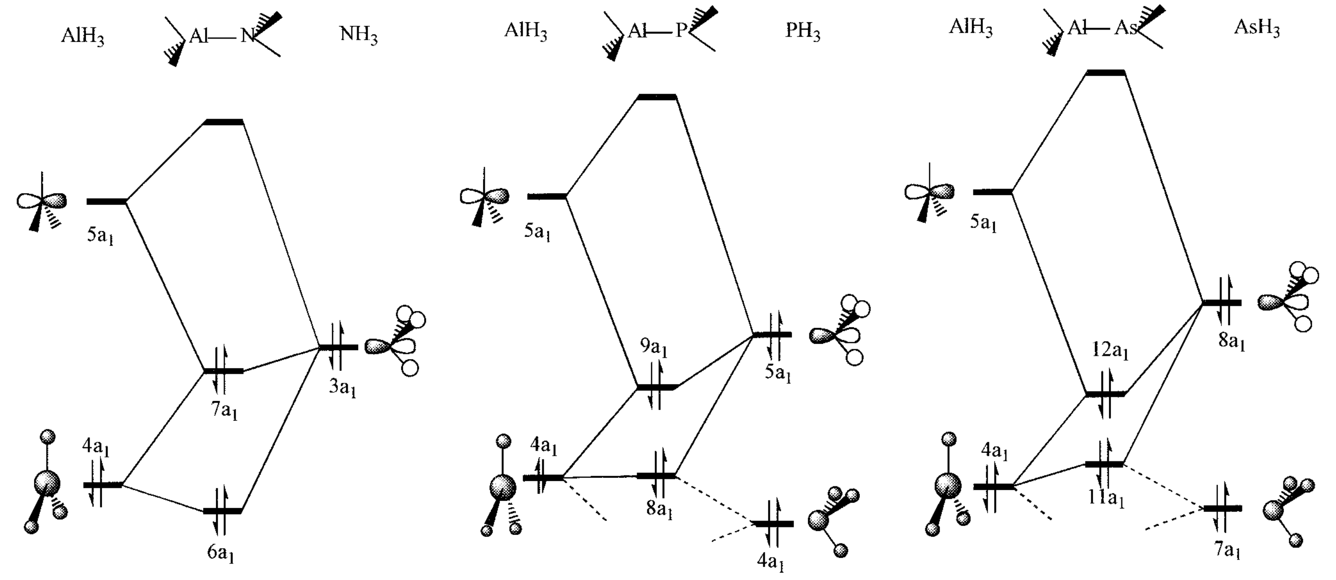


**Figure 1.** Linear correlation between G2(MP2) proton affinities and the complexation energies of (a) $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and (b) $H_3AlYH_3$ (Y = N, P, and As) complexes.



(a) (b) (c)

**Figure 2.** Fragmental analysis of the "$a_1$" symmetry molecular orbitals of (a) $H_3AlNH_3$, (b) $H_3AlPH_3$, and (c) $H_3AlAsH_3$.

tively, and the HOMO orbital of the anionic ligands is close to the $AlH_3$ LUMO one. Furthermore, in the anionic complexes, the central atom X of the donor is in its preferred coordination.

To our knowledge, no correlation has been discussed for the donor−acceptor complexes of alane. However, for the boron ones, there are many relationships available.[30−34,42−46] The proton affinity (as to what was mentioned above) can be taken as a quantitative measure of the charge transferred to the aluminum hydride from the ligand (Lewis bases). In parts a and b of Figure 1, we present the linear correlation between the proton affinities of the ligand, $[XH_3]^-$ and $YH_3$, and the complexation energies of $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and $H_3AlYH_3$ (Y = N, P, and As). This correlation reflects that the stability of the complex depends on the nature of ligand, which increases when the basicity of the Lewis bases increases.

On the other hand, one can see, from the NBO-MP2(full)/6-31G(d) analysis (Table 4), that there is no correlation between charge transfer and the G2(MP2) complexation energy for the two series of complexes, as recently reported.[30−34,47] For the most stable anionic complex $[H_3AlCH_3]^-$, the charge transferred is 0.338e, while for the less stable one $[H_3AlGeH_3]^-$ this charge is 0.536e. We note also the same trend for the neutral complexes.

**3.3. Modes of Coordination.** In this section, we will not discuss the coordination mode of the anionic compounds $[H_3AlXH_3]^-$ (X = C, Si, and Ge) because it is based on a classical HOMO−LUMO interaction mode which is well known. The energetic information given in Table 3 brings out several questions. What is the origin of the stabilization upon complexation? Why is the $H_3AlNH_3$ complex more stable than the $H_3AlPH_3$ and $H_3AlAsH_3$ ones, although all ligands have the same number of valence electrons and the same hybridization for the base center, Y ($sp^3$)? The answers to these questions are directly related to the molecular orbital redistribution, which takes place upon coordination. In this section, we apply QMOA to examine the factors behind the stabilization upon coordination and show which fragment orbitals are implicated in the construction bond between aluminum and Y atoms (Y = central atom of the donor fragment). The characteristics of the chemical bond in the complexes will be discussed under consideration from ab initio calculations at the HF/STO-3G level of theory (this basis set has been chosen only for qualitative investigations). In all correlation diagrams, the molecular orbitals of alane $AlH_3$ and the ligands ($NH_3$, $PH_3$, and $AsH_3$) were taken in the symmetry of the corresponding complexes.

For all compounds, the complexation is controlled by the presence of two interaction types. The first one takes place between the "$a_1$" symmetry orbital likely to interact along the axis of the Al−Y bond (i.e., a three-level and four-electron model system),[30] and the second one uses the "e" symmetry orbitals whose character is rather destabilizing because they are all occupied.

Parts a−c of Figure 2 illustrate the fragmental analysis of "$a_1$" symmetry molecular orbitals that generally influence the molecular bonding of $H_3AlNH_3$, $H_3AlPH_3$, and $H_3AlAsH_3$, respectively. In this interaction type, the systems stabilization depends mainly on the energy position of the intermediate orbital of the compounds compared to the highest fragment occupied one. In fact, the system is stabilized when its intermediate orbital is energetically lower than the highest occupied of the three interacting ones, while in the contrary case, the system is destabilized. These two characters are directly related to the "binding mixture-antibinding mixture" ratio of the intermediate fragment orbital with the highest and the lowest ones, respectively.[48,49] When the binding character overrides on the antibinding character, the intermediate MO of the complex is lower than the fragment intermediate one. This is reversed when the antibinding character is the prevailing. In our case, the molecular orbitals $ma_1$ ($m = 7$, 9, and 12 for $H_3AlNH_3$, $H_3AlPH_3$, and $H_3AlAsH_3$ respectively) are lower than the $na_1$ ($n = 3$, 5, and 8) donor orbitals. It has, consequently, a binding character which increases in going from $H_3AlNH_3$ to $H_3AlAsH_3$ because the corresponding energetic gap ($E(5a_1(ALH_3)) - E(na_1(\text{donor}))$; $n = 3$, 5, and 8) decreases in the same order (0.688, 0.628, and 0.616 au, respectively). This favors the two fragments binding.

However, if we take into account only these three interacting orbitals, the energetic level of the lowest $m'a_1$ ($m' = 6$, 8, and 11 for $H_3AlNH_3$, $H_3AlPH_3$, and $H_3AlAsH_3$, respectively) molecular orbitals of the complexes resulting from this interaction would be more stable than the $AlH_3$ "$4a_1$" one. Our results show that the "$6a_1$" molecular orbital adduct level is energetically slightly lower than the "$4a_1$" one for $H_3AlNH_3$ (Figure 2a). Whereas for the two other complexes ($H_3AlPH_3$ and $H_3AlAsH_3$) $m'a_1$ ($m' = 7$ and 11 respectively) molecular orbital levels are higher than "$4a_1$" (parts b and c of Figure 2). This

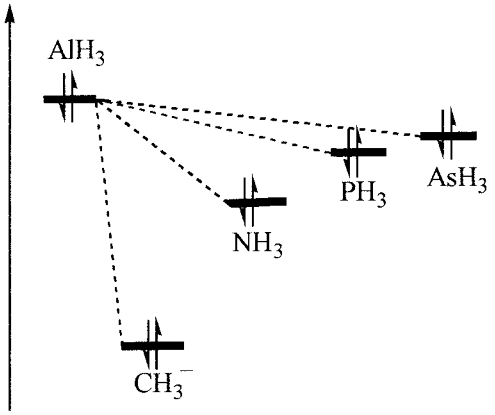


**Figure 3.** "e" symmetry MO energy level diagram for $AlH_3$ and $YH_3$ (Y = N, P, and As) and $[CH3]^-$.

anomaly is due to a notable antibinding perturbation caused by the second occupied $n'a_1$ orbital ($n' = 2$, 4, and 7 for $NH_3$, $PH_3$, and $AsH_3$, respectively) of the donor fragment. This perturbation is destabilizing and its force depends on the energetic position of the donor $n'a_1$ orbital, compared to the $4a_1$ of the fragment acceptor. This orbital is energetically deeper in the $NH_3$ case, but it is close to the $4a_1$ one in the two other cases. In fact, the energetic difference ($E(4a_1) - E(n'a_1)$; $n' = 2$, 4, and 7) is about 15.0, 0.28, and 0.25 au at the HF/STO-3G level of theory for the $NH_3$, $PH_3$, and $AsH_3$ fragments, respectively.

The others interaction types, which must be taken into account, are the "e" symmetry orbital ones. These orbitals are all occupied, and their mixture with themselves is well-known to be destabilizing (mixture of two orbitals occupied by four electrons).[36] The force of this destabilizing interaction depends on the energetic gap $E$("e"(acceptor)) − $E$("e" (donor)). Figure 3 illustrates the evolution energy of the "e" symmetry molecular orbital of $AlH_3$ and $YH_3$ (Y = N, P, and As) which decreases in going from $NH_3$ to $AsH_3$. To compare those fragment orbital levels, we also have reported the $[CH_3]^-$ one for which the "e" symmetry orbital interacts slightly with the alane one. Indeed, at the STO-3G level of theory, this energetic gap is about 0.21, 0.11, and 0.10 au for $NH_3$, $PH_3$, and $AsH_3$ fragments, respectively. Thus, the contributions of the "e" symmetry destabilizing interactions result in a decrease in the stability of complex.

The tree types of interactions ("$a_1$" and "e" symmetry) implicated in the bond construction between the acceptor $AlH_3$ and the donor $YH_3$ (Y = N, P, and As) have one stabilizing character and one or two destabilizing others. These characters stabilizing and destabilizing are irregularly compensated with themselves. These tree interaction types justify the trend obtained by the G2(MP2) calculated complexation energies (Table 4).

## 4. Conclusion

In this work, we have shown that both $[H_3AlXH_3]^-$ (X = C, Si, and Ge) and $H_3AlYH_3$ (Y = N, P, and As) complexes prefer the staggered conformation. The G2(MP2) results show that the anionic complexes are more stable than the neutral ones. The qualitative molecular orbital analysis (QMOA) shows that the mode of coordination is a result of two interactions types. The first one is between the "$a_1$" symmetry fragments orbitals, and the second one is between the "e" symmetry fragments orbitals. The first interaction has a stabilizing character, while the second one is destabilizing. In the anionic complexes, the mode of coordination is controlled mainly by a simple HOMO−LUMO interaction. Thus, in the neutral complexes, the bonding can be classified as pseudocovalent type of bond, but in the anionic complexes, the bonding is covalent. The calculated G2(MP2) complexation energy decreases in the two series. This is a consequence of an irregular variation of the energetic gap between the interacting fragment orbitals. However, this complexation energy varies linearly with the proton affinity, but there is no correlation with the charge transfer.

## References and Notes

(1) Hassanzadeh, P.; Citra, A.; Andrews, L.; Neurock, M. *J. Phys. Chem.* **1996**, *100*, 7317.
(2) Suelson, A. *J. Phys. Chem.* **1967**, *71*, 3202.
(3) SamSonov, E. D.; Osin, S. B.; Shevel'kov, V. F. *Russ. J. Inorg. Chem.* **1988**, *33*, 1598.
(4) Lesiecki, M. L.; Shirk, J. S. *J. Chem. Phys.* **1972**, *56*, 4171.
(5) Schnockel, H. *Z. Anorg. Allg. Chem. Phys.* **1976**, *424*, 203.
(6) Beattic, I. R.; Blayden, H. E.; Ogden, J. S. *J. Chem. Phys.* **1976**, *64*, 909.
(7) Shirk, J. S.; Shirk, A. E. *J. Chem. Phys.* **1976**, *64*, 910.
(8) Wilson, M.; Coolidge, M. B.; Mains, G. J. *J. Phys. Chem.* **1992**, *96*, 4851.
(9) Pong, R. G. S.; Shirk, A. E.; Shirk, J. S. *J. Chem. Phys.* **1979**, *70*, 525.
(10) Sjoegren, C. E.; Klacboc, P.; Ryther, E. *Spectrochim. Acta* **1984**, *40A*, 457.
(11) Jasien, P. G. *J. Phys. Chem.* **1992**, *96*, 9273.
(12) LePage, T. J.; Wiberg, K. B. *J. Am. Chem. Soc.* **1988**, *110*, 6642.
(13) Cannolly, J. W.; Dudis, D. S. *Macromolecules* **1994**, *27*, 1423.
(14) Ball, D. W. *J. Phys. Chem.* **1995**, *99*, 12786.
(15) Gropen, O.; Johansen, R.; Haaland, A.; Stokeland, O. *J. Organomet. Chem.* **1975**, *92*, 147.
(16) Papatheodorou, G. N.; Curtiss, L. A.; Maroni, V. A. *J. Chem. Phys.* **1983**, *78*, 3303.
(17) Winkler, A.; Resh, Ch.; Rendulic, K. D. *J. Chem. Phys.* **1935**, *21*, 992.
(18) Dou, D.; Ketchum, D. R.; Hamilton, E. J. M.; Florian, P. A.; Vermillon, K. E.; Grandinetti, P. J.; Shore, S. G. *Chem. Mater.* **1996**, *8*, 2839.
(19) Sakai, S. *J. Phys. Chem.* **1991**, *95*, 175.
(20) Sakai, S. *J. Phys. Chem.* **1991**, *95*, 7089.
(21) Bates, S.; Dwyer, J. *J. Phys. Chem.* **1993**, *97*, 5897.
(22) Edwards, A. H.; Jones, K. A. *J. Chem. Phys.* **1991**, *94*, 2894.
(23) Che, J.; Choe, H.-S.; Chook, Y.-M.; Jensen, E.; Seida, P. R.; Franci, M. M. *Organometallics* **1990**, *9*, 2309.
(24) Atwood, J. L.; Bennett, F. R.; Elms, F. M.; Jones, C.; Raston, C. L.; Robinson, K. D. *J. Am. Chem.* Soc. **1991**, *113*, 8183.
(25) Marsh, C. M. B.; Hamilton, T. P.; Xie Y.; Schaefer, H. F., III *J. Chem. Phys.* **1992**, *96*, 5310.
(26) Haaland, A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 992.
(27) Jungwirth, P.; Zahradník, R. *J. Mol. Struct. (THEOCHEM)* **1993**, *283*, 317.
(28) Branchadell, V.; Sbai, A.; Oliva, A. *J. Phys. Chem.* **1995**, *99*, 6472.
(29) Jarid, A.; Boutalib, A. Unpublished results.
(30) Anane, H.; Boutalib, A.; Tomás, F. *J. Phys. Chem. A* **1997**, *101*, 7879.
(31) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *Chem. Phys. Lett.* **1998**, *287*, 757.
(32) Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *Chem. Phys. Lett.* **1998**, *296*, 277.
(33) Anane, H.; Jarid, A.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *J. Mol. Struct. (THEOCHEM)* **1998**, *455*, 51.
(34) Anane, H.; Boutalib, A.; Nebot-Gil, I.; Tomás, F. *J. Phys. Chem. A* **1998**, *102*, 7070.
(35) Lowe, J. P. *Quantum Chemistry*; Academic Press: New York, 1978.
(36) Gimarc, B. M. *Molecular Structure and Bonding*; Academic Press: New York, 1979.
(37) Frisch, M. J.; Trucks, G. W.; Head-Gorden, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Rahavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; Defrees, D. J.; Stewart, J. J. P.; Pople, J. A. *GAUSSIAN 92*; Gaussian, Inc.: Pittsburgh, PA, 1992.
(38) Curtiss, L. A.; Ragavachari, K.; Pople, J. A. *J. Chem. Phys.* **1993**, *98*, 1293.
(39) Pople, J. A.; Schlegel, H. B.; Binkly, J. S.; Frisch, M. J.; Whitside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269.
(40) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 269.

(41) Pauling, L. *J. Am. Chem. Soc*. **1947**, 69, 542.

(42) Rice, B.; Galiano, R. J.; Lehmann, W. J. *J. Phys. Chem*. **1957**, *61*, 1222.

(43) Phillips, W. D.; Miller, H. C.; Muetterties, E. L. *J. Am. Chem*. Soc. **1959**, *81*, 4496.

(44) Gutowsky, H. S.; McCall, O. W.; Slichter, C. P. *J. Am. Chem. Soc*. **1953**, *75*, 4496.

(45) Onak, T. P.; Landesman, H.; Williams, R. E.; Shapiro, I. *J. Phys. Chem*. **1959**, *63*, 1533.

(46) Watanabe, H.; Nagasawa, K. *Inorg. Chem.* **1967**, *6*, 1068.

(47) Dapprich, S.; Frenking, G. *J. Phys. Chem*. **1996**, *99*, 9352.

(48) Albright, T. A.; Burdett, J. K.; Whangbo, M.-H. *Orbital Interactions in Chemistry*; John Wiley: New York, 1985; p 32.

(49) Jean, Y.; Volatron, F. *Les Orbitales Moléculaires en Chimie, Introduction et Application*; McGraw-Hill: Paris, 1991; p 156.