G2 Molecular Orbital Investigation of Torsional Barriers in $H_2Al{=}XHCH_3$ and $H_2Al{=}YCH_3$ (X = N, P, and As; Y = O, S, and Se) Systems

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Received: March 28, 2003; In Final Form: May 28, 2003

Structures of $H_2Al{=}XHCH_3$ and $H_2Al{=}YCH_3$ (X = N, P, and As; Y = O, S, and Se) systems were investigated using ab initio method at the G2 level to study the conformational preferences of the methyl group. In all of the molecules, the eclipsed C_s symmetry arrangement (one of the C−H bonds of the methyl group eclipses Al═X(Y)) conformer is found to be more stable than the staggered C_s symmetry arrangement (the C−H bond is trans to Al═X(Y))conformer. The G2 energetic results show that the 3-fold methyl rotational barrier is found to decrease as the electronegativity of X(Y) increases. They also show that this 3-fold methyl rotational barrier decreases when descending in the corresponding periodic table column, from nitrogen (or oxygen) to arsenic (or selenium) atoms. A qualitative argument based on the interaction of the fragment orbitals is used to rationalize the observed trends. The thermodynamic values of the methyl transfer reactions are examined. The possible dissociation processes of $H_2Al{=}XH(Y)CH_3$ systems into HAlXH(Y) and CH_4 or into $HAlXCH_3$ and molecular H_2 are also examined and reported.

1. Introduction

Chemical vapor deposition (CVD) of aluminum and aluminum compounds is of interest for a variety of technologies. For example, CVD remains today one of the most attractive methods to prepare AlN solid films which has many interesting properties such as high thermal conductivity, good oxidation resistance and hard coatings for abrasion and corrosion resistance, among others, which make it a promising material for future years.[1−5] Therefore, reactions of base-stabilized AlH_3 with secondary amines R_2NH were studied in detail in order to obtain structural information on as-prepared oligomeric aminoalanes. The reaction temperature, the stoichiometry of the reactants, and the steric demand of the substituent bound to N were found to play key roles in what degree of oligomerization was attained. Monomeric aminoalanes of the type base $Al(H_2)NR_2$ as well as oligomeric aminoalanes such as $[H_2AlNR_2]_x$ were obtained, mainly in the form of a four-membered heterocycle.[6−14] In contrast, equimolecular reactions of H_3AlNR_3 donor acceptor complex with primary amines RNH_2 preferentially yielded iminoalanes rather than aminoalanes $[H_2AlN(H)R]_x$, depending on their instability toward further H_2 elimination reactions. Aminoalanes of the type $H_2AlN(H)R$ are only known in the form of intramolecular stabilized heterocycles.[13,14] On the other hand, donor acceptor complexes of Lewis acids AlH_3 and AlX_3 (X = halogen atom) with various Lewis bases have been the subject of many experimental and theoretical studies.[15−28] Recently, we reported detailed ab initio molecular orbital studies of a series of donor−acceptor complexes of AlH_3.[29−34] We showed that the stability of these complexes does not depends on the charge transfer. We have also shown that the donor−acceptor coordination was not based on a simple HOMO−LUMO interaction.

In this work, we have now extended our investigation to the structures and energetics of the conformations of $H_2Al{=}XHCH_3$ and $H_2Al{=}YCH_3$ (X = N, P, and As; Y = O, S, and Se) systems by ab initio calculations. The relative stability and 3-fold methyl rotational barrier of these systems are examined. The possible dissociation of the $H_2Al{=}XH(Y)CH_3$ systems into HAlXH(Y) and CH_4 and the dissociation of the $H_2Al{=}XHCH_3$ systems into $HAlXCH_3$ and molecular H_2 are examined. In addition, methyl transfer reactions are also examined. To the best of our knowledge, no comparative ab initio study of these systems has been carried out.

2. Computational Details

Ab initio calculations were performed using the Gaussian 98 program.[35] Geometry optimizations were performed at the MP2-(full)/6-31G(d) level.[36] No symmetry constraints were imposed during the optimization process, and the geometry searches were carried out for a number of possible isomers to ensure the location of the global minimum. The zero-point vibrational energies (ZPE) are obtained from scaled HF/6-31G (d) calculated frequencies (scaled by the factor 0.893).[37] For improved energy, the Gaussian-2 (G2) energies[38] were computed.

3. Results and Discussion

The methyl group in **1**−**7** (C_s symmetry systems) has two conformational eclipsed and staggered orientations (Figure 1). In **1a**−**7a**, one of the C−H bonds of the methyl group eclipses the double bond (eclipsed conformation), and in **1b**−**7b**, the C−H bond is trans to the double bond (staggered conformation). **1a**−**3a**, **5a**, and **7a** correspond to minima and **1b**−**3b**, **5b**, and

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10.1021/jp034809k CCC: $25.00

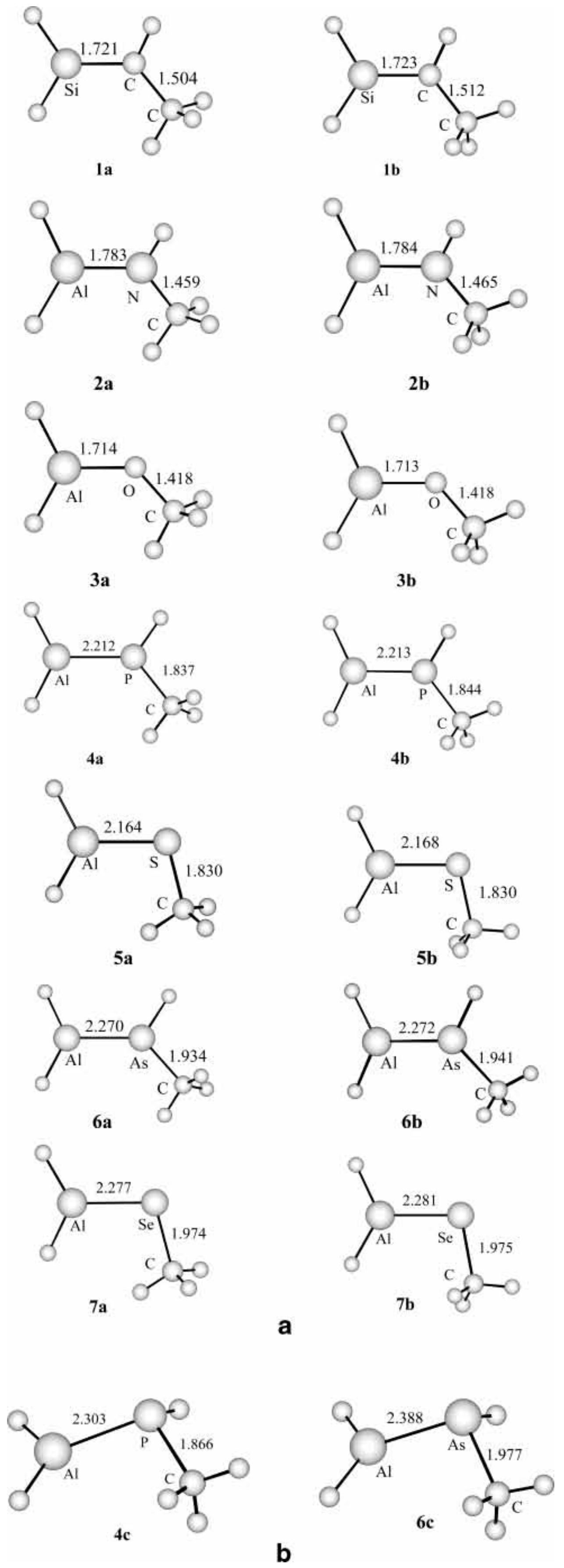

Figure 1. Optimized Structures of (a) C_s symmetry **1**−**7** and (b) C_1 symmetry **4c** and **6c** molecules. Distances are in angstroms.

TABLE 1: Total (a.u.), Relative Energies (kcal/mol) and Entropies (298 K, 1 atm, Ideal Gas − cal/(mol K)), and Thermal Corrections to the Internal Energy (kcal/mol) for 1−7

	total energy (NIM)[a]	relative energy	entropy	thermal
1a	−368.63635(0)	0.0	67.38	2.92
1b	−368.63353(1)	1.96	65.41	2.59
2a	−338.29202(0)	0.0	69.21	3.18
2b	−338.28969(1)	1.46	67.17	2.86
3a	−358.17394(0)	0.0	70.82	3.29
3b	−358.17320(1)	0.46	67.41	2.85
4a	−624.49691(1)	0.0	72.77	3.38
4b	−624.49538(2)	0.96	70.22	2.99
4c	−624.50617(0)	−5.81	75.26	3.72
5a	−680.77749(0)	0.0	76.16	3.50
5b	−680.77701(1)	0.30	70.18	2.98
6a	−2517.89355(1)	0.0	75.55	3.51
6b	−2517.89252(2)	0.65	72.87	3.11
6c	−2517.90906(0)	−9.73	78.76	3.90
7a	−2683.02177(0)	0.0	76.75	3.56
7b	−2683.02161(1)	0.10	73.35	3.12

[a] The values in parentheses correspond to the number of imaginary frequencies.

7b, to transition states. **4a** and **6a** and **4b** and **5b** are characterized to higher order stationary points, order one and two, respectively (Table 1). The energy difference between the two conformations gives the 3-fold methyl rotational barrier. The origin of the methyl rotational barrier in $H_2Al{=}X{-}CH_3$ (X = NH and O), $H_2Al{=}X{-}CH_3$ (X = PH and S), and $H_2Al{=}X{-}CH_3$ (X = AsH and Se) can be extended from that closely related isoelectronic species, $H_2Si{=}CH{-}CH_3$ (**1**). The relative stability of the eclipsed conformations over the staggered ones of these systems are examined with respect to the qualitative molecular orbital analysis (QMOA).[39,40] The QMOA arguments have proved useful and successful for predicting the broad outlines of calculations. They enhance understanding of the relationship between the approximate orbitals we visualize and the detailed results produced by the ab initio calculations.

For the sake of simplicity and because the lowest energy conformation of the methyl group in **2**−**7** remains in the same order as that of **1**, an explanation similar to that in **1** can be applied here also. Indeed, a fragment molecular orbital analysis was carried out at the HF/STO-3G level of theory on the MP2-(full)/6-31G(d)-optimized geometries (this basis set has been chosen only for qualitative investigations).

Figure 2 illustrates the fragmental analysis of molecular orbitals that generally influences the stability of the eclipsed conformation over the staggered one. Consequently, the preference of C_s structures **2a**−**7a** can be rationalized in terms of the interactions of the π orbitals of the double bond (π_{db}) with the pseudo-π orbitals of the methyl group (π_{Me}) similar to that illustrated in Figure 2. These orbitals are all occupied, and their mixture is a well-known destabilizing interaction (i.e., a two level and four-electron model system). The bonding combination ($\pi_{db} + \pi_{Me}$) leads to the stabilization and strengthening of the $C_{Me}{-}H$ and $X{-}C_{Me}$ bond. On the other hand, the antibonding combination ($\pi_{db} - \pi_{Me}$) weakens the $X{-}C_{Me}$ bond. Further, there is a repulsive interaction between the pπ-orbital on Al and the H 1s orbital of the methyl group which are nonbonded (Figure 2). The repulsive antibonding combination of these two components dominates in the staggered conformation, whereas in the eclipsed conformation this destabilizing interaction is reduced because the pseudo-π_{Me} orbitals are directed away from the π_{db} bond orbitals. However, if we take into account these bonding and antibonding interacting orbitals, it has, conse-

TABLE 2: G2 Calculated Thermodynamic Values (in kcal/mol) of the Dissociation Process of 2−7 Systems

dissociation process	ΔE_0	ΔH_0	ΔG_{298}
$H_2AlNHCH_3 \rightarrow HAlNCH_3 + H_2$	+57.36	+59.04	+51.51
$H_2AlNHCH_3 \rightarrow HAlNH + CH_4$	+38.39	+39.68	+30.99
$H_2AlPHCH_3 \rightarrow HAlPCH_3 + H_2$	+37.40	+39.03	+30.16
$H_2AlPHCH_3 \rightarrow HAlPH + CH_4$	+18.44	+19.40	+10.33
$H_2AlAsHCH_3 \rightarrow HAlAsCH_3 + H_2$	+31.59	+33.0	+24.96
$H_2AlAsHCH_3 \rightarrow HAlAsH + CH_4$	+13.29	+14.06	+5.31
$H_2AlOCH_3 \rightarrow HAlO + CH_4$	+28.59	+29.43	+21.91
$H_2AlSCH_3 \rightarrow HAlS + CH_4$	+5.12	+5.76	−0.98
$H_2AlSeCH_3 \rightarrow HAlSe + CH_4$	+1.19	+1.74	+0.11

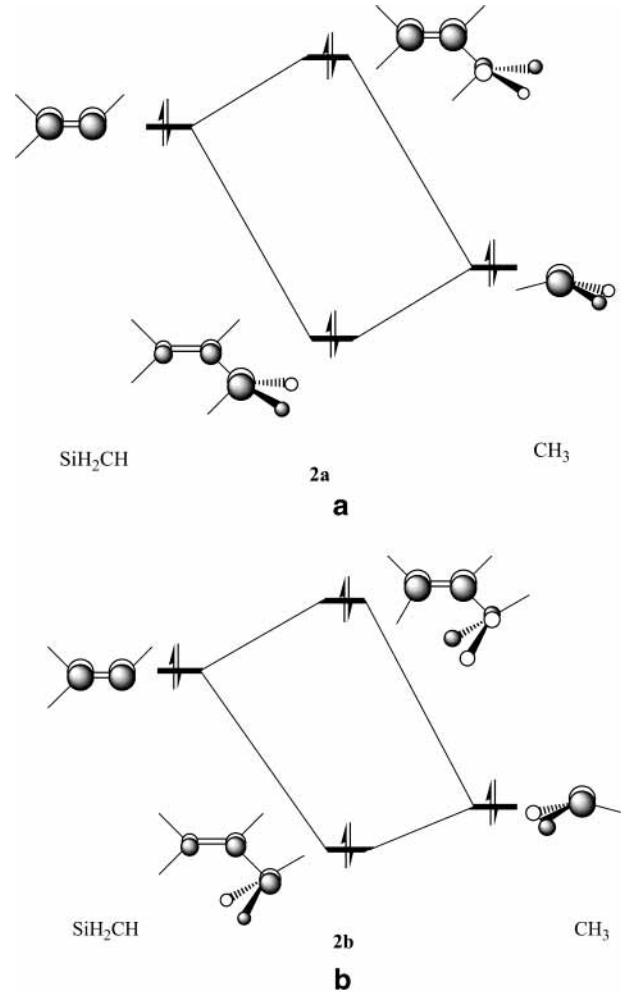

Figure 2. Schematic interaction diagram of the occupied π orbital of the double bond with the methyl group in (a) **1a** and (b) **1b**.

TABLE 3: G2 Calculated Thermodynamic Values (in kcal/mol) of the Methyl Transfer Process of 2−7 Systems

methyl transfer process	ΔE_0	ΔH_0	ΔG_{298}
$H_2AlNH_2 + CH_3NH_2 \rightarrow H_2AlNHCH_3 + NH_3$	−0.72	−0.29	+0.15
$H_2AlPH_2 + CH_3PH_2 \rightarrow H_2AlPHCH_3 + PH_3$	−1.27	−0.97	−0.58
$H_2AlAsH_2 + CH_3AsH_2 \rightarrow H_2AlAsHCH_3 + AsH_3$	−0.36	−0.09	+0.30
$H_2AlOH + CH_3OH \rightarrow H_2AlOCH_3 + OH_2$	−0.67	+0.04	+0.22
$H_2AlSH + CH_3SH \rightarrow H_2AlSCH_3 + SH_2$	+0.62	+1.20	+0.76
$H_2AlSeH + CH_3SeH \rightarrow H_2AlSeCH_3 + SeH_2$	+0.52	+0.99	+1.29

quently, a slightly longer X−C_{Me} bond distance in **1b**−**7b** than in **1a**−**7a**.

On the other hand, the methyl rotational barrier is found to decrease on going from **1** to **3**, **4** to **5**, and **6** to **7** (Table 1). Indeed, the double bond is polarized because of the electronegativity difference between aluminum and the heteroatom (N, P, As, O, S, and Se), and hence, the electrons are more or less localized on the heteroatom. This can be seen from the MO pattern, which shows a smaller coefficient size on the aluminum p_π-orbital compared to the heteroatom p_π orbital. As a result, the antibonding interaction between the H 1s orbital on π_{Me} and the p_π orbital on aluminum is reduced substantially.

Let us now examine the structural behavior around the phosphorus and arsenic atoms in **4** and **6** molecules, respectively. Table 1 shows that, though a barrier exists between **4a** and **4b** and between **6a** and **6b**, respectively, both are characterized to be higher order stationary points. This observation is in striking contrast to that of its congener **2a**, which is found to be a minimum. The bondings in **4c** and **6c** are different from that of **4a**−**b** and **6a**−**b**. The Al−X (X = P, As) bonds in **4c** and **6c** are longer compared respectively to those in **4a** and **6a** and more close to a single Al−X bond rather than an Al−X double bond (Figure 1). Thus, the environment around phosphorus and arsenic in **4c** and **6c** is pyramidal whereas in **4a**−**b** and **6a**−**b**, it is planar. The stability of **4c** and **6c** over **4a**−**b** and **6a**−**b**, respectively, indicates that the stronger preference in energy between **4a** and **4c** (−5.81 kcal/mol) and between **6a** and **6c** (−9.73 kcal/mol) gives the barrier to planarity of **4c** and **6c**.

On an other side, the calculated thermodynamic values of methane elimination as well as molecular H_2 elimination are reported in Table 2. Indeed, for the $H_2AlXHCH_3$ systems, we have taken into account two possible elimination reactions. The elimination of methane or molecular H_2 leads to HAlXH as well as $HAlXCH_3$, respectively. For the H_2AlYCH_3 systems, we have taken into account the elimination of methane leading to HAlY systems. Thus, the dissociations of $H_2AlXHCH_3$ into HAlXH and CH_4 or $HAlXCH_3$ and molecular H_2 are endothermic. The dissociation of H_2AlYCH_3 into HAlY and CH_4 is also endothermic (Table 2). There is a clear decrease in the magnitude of the elimination processes when descending in the corresponding periodic table column, from nitrogen (or oxygen) to arsenic (or selenium) atoms. The magnitudes are considerably less in the case of third row X(Y). The same trend is observed at room temperature (298 K). The endothermicties of the above reactions indicate that the methyl group stabilizes the Al═X bond and the systems are stable over the elimination of CH_4 or molecular H_2. Thus, the elimination of CH_4 or molecular H_2 is less favorable.

On the other hand, a series of methyl transfer reactions were considered to account for the effect of methyl substitution on the heteroatom. The corresponding thermodynamic values are reported in Table 3. As one can see, from the thermodynamic reported values that the methyl group stabilizes the Al═X bond rather than the Al═Y bond. There is a sensitive decrease of the stabilization energy with increasing electronegativity. The same trends are observed at room temperature.

4. Conclusion

In this work, we have shown that the conformations of the methyl group in the $H_2Al{=}XHCH_3$ and $H_2Al{=}YCH_3$ (X = N, P, and As; Y = O, S, and Se) systems prefer the eclipsed C_s

symmetry arrangement (one of the C−H bonds of the methyl group eclipses Al═X(Y)). The G2 energetic results show that the 3-fold methyl rotational barrier is found to decrease as the electronegativity of X(Y) increases. They also show that this 3-fold methyl rotational barrier decreases when descending in the corresponding periodic table column, from nitrogen (or oxygen) to arsenic (or selenium) atoms. The qualitative molecular orbital analysis (QMOA) rationalizes the observed trends. The possible dissociation processes of $H_2Al{=}XH(Y)CH_3$ systems into HAlXH(Y) and CH_4 or into $HAlXCH_3$ and molecular H_2 are endothermic. The thermodynamic values of the methyl transfer reactions are slightly exothermic. These observations indicate that $H_2Al{=}XH(Y)CH_3$ systems are stabilized by transfer of the methyl group.

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