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Theoretical Investigation of Alane−$NH_{3-n}F_n$ and Alane−$NH_{3-n}Cl_n$ ($n = 0-3$) Interactions

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The alane−$NH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) donor−acceptor complexes have been investigated at the G2(MP2) level of theory. The G2(MP2) results show that the successive fluorine and chlorine substitution on the nitrogen decreases the stability of $H_3AlNH_{3-n}F_n$ and $H_3AlNH_{3-n}Cl_n$ complexes although the basicity of the $NH_{3-n}F_n$ and $NH_{3-n}Cl_n$ ligands decreases with this substitution. The NBO partitioning scheme shows that the shortening of the N−F and N−Cl bond lengths, upon complexation, is due to an increasing "s" character in these bonds. A linear relationship between the G2(MP2) complexation energy and the G2(MP2) proton affinity of the corresponding Lewis bases has been established and discussed.

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 where the aluminum trichloride acts as catalyst. Many of these important compounds have been experimentally and theoretically studied.[1−6] Accurate knowledge of the thermodynamics of complexation energies would serve as a useful framework from which to build a detailed and quantitative understanding of the reactivity and reaction mechanism were alanes are involved.

Numerous studies have been devoted to these type of compounds concerning their structural parameters, the nature of their bonding, their stability, and other physical and chemical properties,[6−15] where the analysis methods differ. Recent theoretical work has been reported about donor−acceptor complexes of phosphorus trihalides with heavier group-13 Lewis acids.[16−18] On the other hand, our group has recently reported the calculated structures of a series of anionic and neutral alane donor−acceptor complexes.[19−22] We showed that the stability of these complexes does not depend on the charge transfer, whereas a correlation between the complexation energy and the corresponding donor fragment proton affinity has been observed. On another hand, we have analyzed the fragment molecular orbitals implied in the coordination process. It has permitted us to know the factors that govern the donor−acceptor interactions and the ones that are behind an irregular evolution of the complexation energy when we change only the central atom of the donor fragment. In continuation of our work, we report now our investigation on the alane−$NH_{3-n}F_n$ and alane−$NH_{3-n}Cl_n$ ($n = 0-3$) donor−acceptor complexes at the G2(MP2) level of theory. To our knowledge, no comparative ab initio studies of these complexes has been carried out. The electronic structure of these complexes has been analyzed and the relative stabilities are examined

2. Computational Details

Ab initio calculations were performed using the GAUSSIAN92 program.[23] Geometry optimizations were performed at the MP2(full)/6-31G(d) level; the zero-point vibrational energies (ZPE) are obtained from scaled HF/6-31G(d) frequencies (scaled by the factor 0.893).[24] For improved energy, the G2(MP2) energies[25] were computed. The charge distribution in the complexes has been analyzed from the natural bond orbital (NBO)[26] partitioning scheme at the MP2(full)/6-31G(d) level. Atomic populations obtained from this analysis are less basis set dependent than those corresponding to the Mulliken population analysis.[26] On another hand, we did not correct for the basis set superposition errors (BSSE), which should be relatively small with a large basis set such as 6-311+G(3df,2p) and have little effect on the calculated complexation energies.[17,27,28]

3. Results and Discussion

First, we have investigated the two possible structures (staggered and eclipsed conformations) for all complexes $H_3AlNH_{3-n}X_n$ ($n = 0-3$; X = F, Cl) at the RHF/ 6-31G(d) level of theory (Figure 1). From calculated frequencies on the optimized geometries, the staggered optimized conformations were characterized as minima and the eclipsed ones were characterized as transition structures for all complexes. All the minima structures have been reinvestigated at the MP2(full)/6-31G(d) level of theory. Completely optimized geometries for all species studied in this work are given in Tables 1 and 2. In Table 3, we have reported the 2s calculated contributions of nitrogen atoms in the N−H, N−F, and N−Cl bonds using the NBO partitioning scheme at the MP2(full)/6-31G(d) level of theory. In Table 4 we give the calculated complexation energies of $H_3AlNH_{3-n}X_n$ ($n = 0-3$) complexes, the proton affinities of $NH_{3-n}X_n$ moieties, and the NBO-MP2(full)/ 6-31G(d) transferred charge from $NH_{3-n}X_n$ Lewis bases to AlH_3 Lewis acid (Q_t). The complexation energies are calculated as the energy difference between the donor−acceptor complex and the respective moieties. The proton affinities (PA) are taken as the energy difference between the neutral and protonated $NH_{3-n}X_n$ Lewis bases. To evaluate the effect of halide substitution, we also give in Table 4 the reported G2(MP2) calculated complexation

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TABLE 1: Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of Free $NH_{3-n}F_3$Ligands and Corresponding Complexes with AlH_3

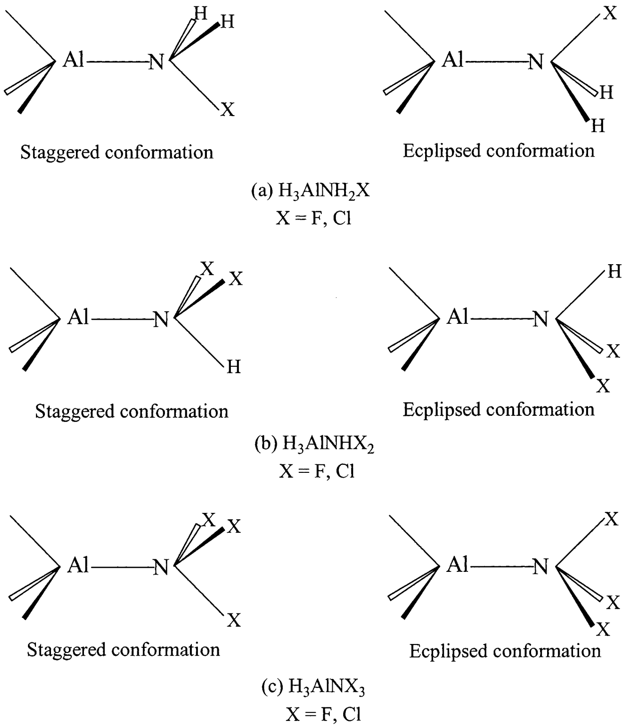
	Al−N	Al−H[a]	N−F	N−H	∠H−Al−N[a]	∠F−N−F	∠F−N−H	∠H−N−H
AlH_3		1.589						
NH_3				1.017				106.35
NH_2F			1.433	1.023			100.92	105.04
NHF_2			1.406	1.028		103.22	99.59	
NF_3			1.383			101.65		
H_3AlNH_3	2.083	1.606		1.020	99.44			107.52
H_3AlNH_2F	2.107	1.611	1.415	1.024	100.74		103.35	107.70
		1.598			90.52			
H_3AlNHF_2	2.174	1.599	1.388	1.029	99.84	104.61	102.33	
		1.591			93.43			
H_3AlNF_3	2.305	1.592	1.369		93.57	103.12		

[a] The second value corresponds to equivalent hydrogen atoms.

TABLE 2: Selected Optimized Bond Lengths (Å) and Bond Angles (deg) of Free $NH_{3-n}Cl_3$Ligands and Corresponding Complexes with AlH_3

	Al−N	Al−H[a]	N−Cl	N−H	∠H−Al−N[a]	∠Cl−N−Cl	∠Cl−N−H	∠H−N−H
AlH_3		1.589						
NH_3				1.017				106.35
NH_2Cl			1.754	1.022			104.43	105.81
$NHCl_2$			1.759	1.027		110.37	102.30	
NCl_3			1.773			107.63		
H_3AlNH_3	2.083	1.606		1.020	99.44			107.52
H_3AlNH_2Cl	2.110	1.610	1.747	1.024	100.43		106.32	106.89
		1.599			92.53			
$H_3AlNHCl_2$	2.155	1.595	1.751	1.028	100.45	111.08	104.46	
		1.601			94.81			
H_3AlNCl_3	2.216	1.596	1.762		95.89	108.43		

[a] The second value corresponds to equivalent hydrogen atoms.



(a) H_3AlNH_2X
X = F, Cl

(b) H_3AlNHX_2
X = F, Cl

(c) H_3AlNX_3
X = F, Cl

Figure 1. Definition and numbering schemes of the geometrical parameters of (a) H_3AlNH_2X, (b) H_3AlNHX_2, and (c) H_3AlNX_3 (X = F, Cl) complexes in staggered and eclipsed conformations.

TABLE 3: 2s MP2-NBO Contributions of Nitrogen Atoms in the N−H, N−F, and N−Cl Bonds (%)

	$ns_{(N-H)}$	$ns_{(N-F)}$		$ns_{(N-H)}$	$ns_{(N-Cl)}$
NH_3	25.17		NH_3	25.17	
NH_2F	24.43	12.73	NH_2Cl	25.78	14.44
NHF_2	23.90	12.59	$NHCl_2$	26.22	14.22
NF_3		12.36	NCl_3	13.54	
H_3AlNH_3	22.72		H_3AlNH_3	22.72	
H_3AlNH_2F	23.47	17.15	H_3AlNH_2Cl	23.48	18.44
H_3AlNHF_2	24.02	19.06	$H_3AlNHCl_2$	24.34	19.59
H_3AlNF_3		21.23	H_3AlNCl_3	16.33	

TABLE 4: G2(MP2) Complexation Energies E_c (kcal/mol) of $H_3AlNH_{3-n}X_n$ (n = 0−3; X = F, Cl) Complexes, Proton Affinities PA (kcal/mol) of $NH_{3-n}X_n$ Ligands, and MP2-NBO Transferred Charge Q_t (e)

$H_3AlNH_{3-n}F_n$ complexes				$H_3AlNH_{3-n}Cl_n$ complexes			
complex	E_c	PA	Q_t	complex	E_c	PA	Q_t
H_3AlNH_3	25.24	202.5	0.16	H_3AlNH_3	25.24	202.5	0.16
H_3AlNH_2F	19.71	181.15	0.14	H_3AlNH_2Cl	20.87	189.42	0.13
H_3AlNHF_2	12.22	158.15	0.12	$H_3AlNHCl_2$	16.46	178.86	0.11
H_3AlNF_3	5.05	132.18	0.09	H_3AlNCl_3	12.89	170.43	0.10

energy and the NBO-MP2(full)/6-31G(d) charge transfer of the parent H_3AlNH_3 donor−acceptor complex.[19]

From Tables 1 and 2, it can be seen that small changes in the N−H and N−X bond distances result from halogen substitution in NH_3. In fact, we observed a lengthening of the N−H bond lengths and a shortening of the N−X ones. The N−H and N−X bonds changes by about 0.01 and 0.03 Å, respectively. Upon complexation, the MP2 calculation shows a small distortion of the N−H and N−X bond lengths. Moreover, this calculation predicts a lengthening of the N−H bond, which seems consistent with a chemical intuition, and a shortening of the N−X bond lengths (Tables 1 and 2). To explain the bonding situation in the alane complexes, we applied the natural bond orbital analysis on theses bonds (Table 3). However, the NBO-MP2(full)/6-31G(d) calculations show that in isolated $NH_{3-n}X_n$ (n = 0−3) moieties the lone pair on donor atom "N" has lower "s" character than in complexes. Hence, we can deduce from these results that this change alone would imply a shortening of the bond lengths due to an increased "s" character in these bonds. Table 3 shows that the 2s atomic orbital (AO) contribu-

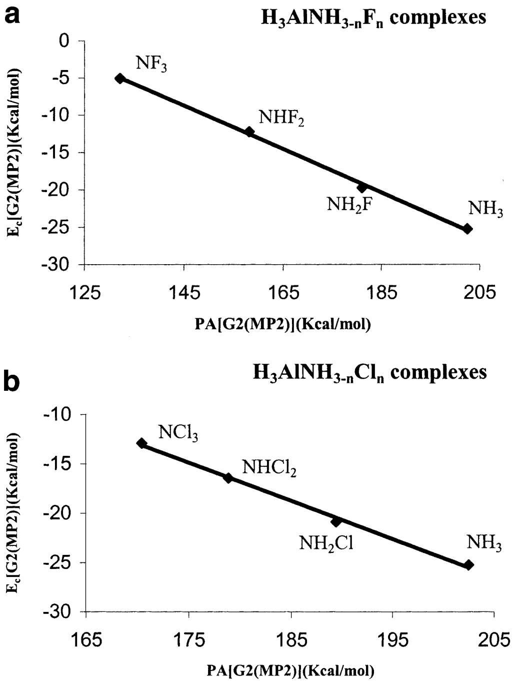


Figure 2. Linear correlation between the G2(MP2) proton affinities and the G2(MP2) complexation energies of (a) $H_3AlNH_{3-n}F_n$ and (b) $H_3AlNH_{3-n}Cl_n$.

tions of N in the N−X bond lengths are more important in $H_3AlNH_{3-n}X_n$ (n = 1−3; X = F, Cl) complexes than in isolated moieties $NH_{3-n}X_n$. Then, we can understand why we had a shortening of the N−X bond length.

The bond angle ∠H−Al−N varies slightly on going from an AlH_3 free moiety (90°) to $H_3AlNH_{3-n}X_n$ complexes. This has a consequence for the Al geometrical environment, which passes from D_{3h} (flat) in free AlH_3 to pseudo-pyramidal in the complexes. For the bond angles ∠X(H)−N−X(H) we note no notable deviation on going from isolated AlH_3 to $H_3AlNH_{3-n}X_n$ complexes. One can see that this bond angle increases by about 2° in going from the isolated $NH_{3-n}X_n$ (n = 0−3; X = F, Cl) ligands to the complex adducts $H_3AlNH_{3-n}X_n$.

On the other hand, the optimized Al−N bond lengths of $H_3AlNH_{3-n}X_n$ (n = 1−3; X = F, Cl) are longer than found in the H_3AlNH_3 complex at the same MP2(full)/ 6-31G(d) level of theory, which indicate weaker Al−N bonding in $H_3AlNH_{3-n}X_n$ (n = 1−3) than in H_3AlNH_3. Indeed the optimized values of Al−N bonds of H_3AlNH_2F, H_3AlNHF_2, and H_3AlNF_3 complexes are 2.107, 2.174, and 2.305 Å, respectively, and of H_3AlNH_2Cl, $H_3AlNHCl_2$, and H_3AlNCl_3 complexes are 2.110, 2.155, and 2.216 Å, respectively. The optimized value of Al−N bond of the H_3AlNH_3 complex is 2.083 Å.[19] One can see, from Table 4, that the lowest complexation energy is obtained for the H_3AlNH_3 complex (−25.24 kcal/mol).

The G2(MP2) calculated complexation energies of $H_3AlNH_{3-n}X_n$ (n = 0−3; X = F, Cl), shown in Table 4, show that the successive fluorine and chlorine substitution on NH_3 decreases the basicity, which is reflected by their calculated G2(MP2) proton affinities and the stability of the corresponding complexes. Indeed, by halogen substitution on the central atom (N) of the donor fragment, the complexation energy, and the charge transfer decrease. This effect is more important upon fluorine substitution. Indeed, fluorine substitution destabilizes the complex by ∼6, ∼13, and ∼20 kcal/mol for H_3AlNH_2F, H_3AlNHF_2, and H_3AlNF_3 complexes, respectively, and chlorine substitution destabilizes the complex only by ∼4, ∼9, and ∼12 kcal/mol for H_3AlNH_2Cl, $H_3AlNHCl_2$, and H_3AlNCl_3 complexes, respectively. The charge-transfer varies according to the complexation energy (Table 4).

On the other hand, we have established a good linear relationship between complexation energy and proton affinity of the Lewis base. In parts a and b of Figure 2, we present the linear correlation between the G2(MP2) proton affinities of the Lewis bases, $NH_{3-n}X_n$ (n = 0−3) (X = F, Cl), and the G2(MP2) complexation energies of $H_3AlNH_{3-n}X_n$ complexes. 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.

4. Conclusion

The substitution effect on ammonia−alane complexes was investigated at the G2(MP2) level of theory. The G2(MP2) results show that the stability of the $H_3AlNH_{3-n}X_n$ (n = 0−3; X = F, Cl) complexes decreases with the degree of the halide substitution at the nitrogen atom. This substitution decreases also the basicity of the $NH_{3-n}X_n$ Lewis bases. Indeed, the complexation energy varies linearly with the G2(MP2) proton affinity of the corresponding Lewis bases. Upon complexation, the MP2(full)/6-31G(d) calculated structural parameters of $H_3AlNH_{3-n}X_n$ complexes show an irregular shortening of N−X (X = F and Cl) bonds. The analysis of the electronic structure using the NBO partitioning scheme shows that this change was related to the contribution rate of the “s” character in these bonds.

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