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Ab initio Investigation of the Substituant Effect of the Alane Complexes

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Ab initio Investigation of the Substituant Effect of the Alane Complexes

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Abstract

Motivation. The binding interactions between an electron pair donor (Lewis base) and an electron pair acceptor (Lewis acid) play an important role in many chemical processes. The reaction course of numerous reactions takes place with formation of donor–acceptor adducts as intermediates. The geometrical parameters are sensitive to intra– and inter–molecular interactions; hence they can indicate and characterize these processes. The strength of the adduct bond is generally lower than that of a typical covalent bond. The present study reports the quantum chemistry analysis of the $X_3AlY(CH_3)_3$ (X = H, F, and Cl; Y = N, P, and As) donor–acceptor complexes.

Method. All calculations were performed with the *ab initio* method at the MP2 level of theory.

Results. For all complexes the staggered conformation (C_{3v} symmetry) is found to be favored. The MP2/6–311++G(df,p) energetic results show that the stability decreases when going from nitrogen to arsenic for all complexes. The NBO partitioning scheme shows that the unusual shortening of the P–C and As–C bond lengths upon complexation is due to an increasing *s* character and Wiberg bond index in these bonds.

Conclusions. The calculated complexation energies corrected with the BSSE corrections show that the $F_3AlY(CH_3)_3$ (Y = N, P, and As) complexes are more stable than $Cl_3AlY(CH_3)_3$ and $H_3AlY(CH_3)_3$ ones. The NBO partitioning scheme analysis shows that there is no correlation between the stability and the charge transfer.

Keywords. *Ab initio* calculation; donor–acceptor complex; stability; substitution; NBO; charge transfer.

1 INTRODUCTION

It is well known that Lewis acids have been known to acts as catalysts in organic reactions. Indeed, there is substantial current interest in adducts based on Group 13 acceptor atoms, such as B, Al or Ga, and Group 15 donor atoms, such as N, P or As. Theses complexes are volatile, readily prepared in high purity and can be decomposed either thermally or by laser irradiation. On the other hand, the types of reactions in which trivalent aluminum plays a catalytic role are many and varied. However, complexes formed by Aluminum trihalides (AlX_3) with various donor systems including

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organic molecules have attracted a lot of attention [1–27]. The points that have been more developed are conformational structure, complexation energy, charge decomposition analysis and degree charge transfer, and the role of the terminal atoms in several donor–acceptor complexes. A recent review about the analysis of the chemical bond in donor–acceptor complexes, including AlX_3, has been reported [28]. Recently, we reported [29] *ab initio* molecular orbital study of X_3AlYH_3 (X = F, Cl, and Br; Y = N, P, and As) complexes. 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. We have also shown that the NH_3 complexes with AlX_3 Lewis acids are more strongly bound than the respective PH_3 and AsH_3 complexes. In continuation of our work, we report now our investigation on the alane–trihalides (AlX_3, X = H, F, and Cl) donor–acceptor complexes $X_3AlY(CH_3)_3$ (Y = N, P, and As). Despite many theoretical works, no comparative *ab initio* studies of these complexes have been carried out. The geometry and electronic structure of these complexes have been analyzed and the relative stability is examined.

2 COMPUTATIONAL DETAILS

The geometry optimizations have been first carried out at Hartree–Fock/6–31+G(d) level. The nature of all stationary point structures were determined by analytical frequency analysis, which also provided zero–point vibrational energies (ZPEs). ZPEs were scaled by the factor 0.9153 [30]. The minima structures were then reoptimized at the MP2/6–311++G(df,p) level. All structures reported here are minima on the potential energy surface (only positive eigenvalues of the Hessian matrix). Final energies were calculated at the MP2/6–311++G(df,p) + ZPEs level. This level of calculation has been recently used successfully by Gilbert on similar complexes [31]. The basis set superposition error (BSSE) correction was evaluated using the counterpoise method [32]. The electronic structure has been done using the natural bond orbital (NBO) partitioning analysis [33]. An important feature of the NBO method is that unlike other charge partitioning schemes, the presence of diffuse functions in the basis sets does not affect the result [33]. The calculations were performed using the GAUSSIAN98 suite of programs [34].

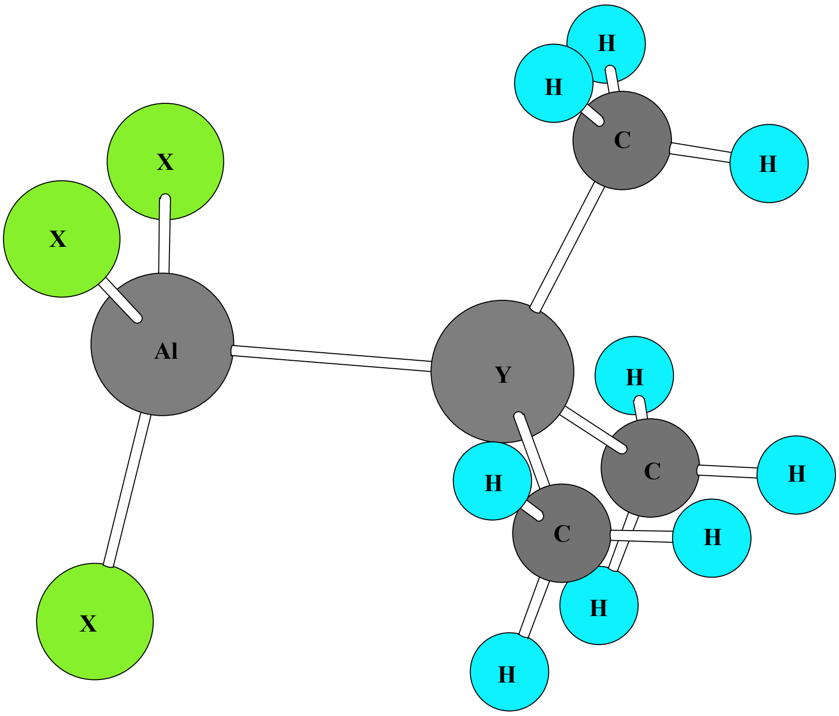
3 RESULTS AND DISCUSSION

Association of AlX_3 (D_{3h} symmetry; X = H, F, and Cl), which act as electron pair acceptors, with $Y(CH_3)_3$ (C_{3v} symmetry; Y = N, P, and As), which act as electron pair donors, leads to $X_3AlY(CH_3)_3$ (C_{3v} symmetry). Table 1 lists relevant optimized bond lengths and bond angles for all the complexes studied in this work. The depicted geometrical parameters are reported in Figure 1.

One can see from Table 1 that upon coordination, there are a number of intramolecular distortions that accompany the formation of the complex. The calculated Al–X bond lengths in $X_3AlY(CH_3)_3$ complexes are much longer than that in isolated moieties AlX_3 (X = H, F, and Cl).

Table 1. MP2/6–311++G(df,p) Calculated Geometries (Bond Length in Å and Bond Angle in Degree)

complex	Al–Y	Al–X	Y–C	∠X–Al–X	∠X–Al–Y or ∠X–Al–C3 axis	∠Al–Y–C	∠C–Y–C
AlH_3		1.578		120.0	90.0		
AlF_3		1.646		120.0	90.0		
$AlCl_3$		2.055		120.0	90.0		
$N(CH_3)_3$			1.449				110.55
$P(CH_3)_3$			1.840				98.94
$As(CH_3)_3$			1.962				96.63
$H_3AlN(CH_3)_3$	2.056	1.601	1.474	117.29	99.59	109.50	109.45
$F_3AlN(CH_3)_3$	1.991	1.676	1.479	116.14	101.48	109.49	109.46
$Cl_3AlN(CH_3)_3$	2.015	2.102	1.483	115.31	102.71	110.29	108.64
$H_3AlP(CH_3)_3$	2.461	1.600	1.820	117.53	99.14	114.53	103.97
$F_3AlP(CH_3)_3$	2.424	1.677	1.816	116.23	101.34	113.55	105.10
$Cl_3AlP(CH_3)_3$	2.407	2.104	1.814	116.20	101.39	113.03	105.69
$H_3AlAs(CH_3)_3$	2.584	1.597	1.939	117.89	98.44	116.41	101.72
$F_3AlAs(CH_3)_3$	2.535	1.675	1.933	116.46	100.98	115.28	103.09
$Cl_3AlAs(CH_3)_3$	2.511	2.102	1.932	116.38	101.11	114.52	103.98



$X_3AlY(CH_3)_3$ C_{3v} Symmetry
(X = H, F, and Cl; Y = N, P, and AS)

Figure 1. Definition of the geometrical parameters of the $X_3AlY(CH_3)_3$ (X = H, F, and Cl; Y= N, P, and As) complexes.

Upon complexation, the lengthening of the Al–X bond increases when going from AlH_3 to $AlCl_3$. This is because in the isolated AlX_3 strong π donation from the halogen lone pairs into the formally empty p(π) orbital at aluminum stabilizes the molecule, yielding shorter Al–X bonds.

Of particular interest is the Y–C (Y = N, P, and As) bond distance. Upon complexation, the calculated geometrical parameters show a lengthening of the N–C bond that seems consistent with a chemical intuition. A striking feature is the shortening of the Y–C (Y = P and As) bonds. Indeed, the NBO calculations show that in isolated donor fragments, the lone pair on Y (Y = P and As) atoms has lower ‘s’ character than that in complexes. Taking into account that greater ‘s’ character in the complex favors a shorter and stronger bond, we can deduce that this change alone would imply a shortening of the Y–C bond lengths because it increases upon coordination. Moreover, Table 2 shows that the 3s and 4s atomic orbital (AO) contribution of P and As respectively, in the P–C and As–C bonds are more important in $X_3AlP(CH_3)_3$ and $X_3AlAs(CH_3)_3$ (X = H, F, and Cl) complexes than that in isolated $P(CH_3)_3$ and $As(CH_3)_3$ moieties. In the even feel, the calculated Wiberg bond index, from the NBO analysis, of the Y–C bond decreases upon coordination for Y = N and increases for Y = P, and As atoms (Table 2).

Table 2. The Optimized Y–C Bond Length of the $Y(CH_3)_3$ Moiety and Their Complexes with AlX_3, Wiberg Bond Index, and the *n*s NBO Contribution of the Y Atom in the Y–C bond

Compound	d(Y–C) (Å)	Wiberg bond index	n_s [a] (%)
$N(CH_3)_3$	1.449	0.9203	28.46
$H_3AlN(CH_3)_3$	1.474	0.8740	26.24
$F_3AlN(CH_3)_3$	1.479	0.8698	27.33
$Cl_3AlN(CH_3)_3$	1.483	0.8622	24.95
$P(CH_3)_3$	1.840	0.8864	17.50
$H_3AlP(CH_3)_3$	1.820	0.9001	23.22
$F_3AlP(CH_3)_33$	1.816	0.9076	25.15
$Cl_3AlP(CH_3)_3$	1.814	0.9056	23.84
$As(CH_3)_3$	1.962	0.8616	14.63
$H_3AlAs(CH_3)_3$	1.939	0.8735	22.66
$F_3AlAs(CH_3)_3$	1.933	0.8820	24.48
$Cl_3AlAs(CH_3)_3$	1.932	0.8794	23.28

[a] *n* = 2, 3, and 4, respectively, for N, P, and As atoms.

On the other hand, the bond angle ∠X–Al–Y (Y = N, P, and As) varies slightly in going from AlX_3 free moiety (90°) to $X_3AlY(CH_3)_3$ complex adduct. It increases only by about 10°. This has a consequence for the Al geometrical environment, which passes from D_{3h} (flat) in free AlX_3 to pseudo–pyramidal in the complex. For the bond angles ∠X–Al–X and ∠C–Y–C we note that no notable deviation in going from isolated AlX_3 to $X_3AlY(CH_3)_3$ complex. One can see that ∠X–Al–X bond angle decreases by about 4° in going from the isolated AlX_3 (X = H, F, and Cl) ligand to the complex adduct. The ∠C–N–C bond angle increases by about ~1–2° in going from the isolated $N(CH_3)_3$ ligand to the complex adduct. The ∠C–P(As)–C bond angle decreases by about ~5–7° in going from the isolated $P(CH_3)_3$ and $As(CH_3)_3$ moieties to the complexes adducts. This trend is consistent with the observed shortening of the P–C and As–C bond lengths.

In order to evaluate the effect of substitution of hydrogen by methyl in all the compounds, we have also calculated the Al–Y bond lengths of the non methylated complexes. Indeed, the optimized Al–Y bond lengths of $H_3AlY(CH_3)_3$ (Y = N, P, and As) complexes are 2.056, 2.461, and 2.584 Å, 0.009, 0.158, and 0.081 Å shorter than that found in H_3AlNH_3, H_3AlPH_3, and H_3AlAsH_3, respectively, at the same MP2/6–311++G(df,p) level of theory which indicate stronger Al–Y bonding in $H_3AlY(CH_3)_3$ than that in H_3AlYH_3. The same trend has been observed for $F_3AlY(CH_3)_3$ and $Cl_3AlY(CH_3)_3$ complexes. These trends show that all the methylated complexes will be more stable than the non–methylated ones. Indeed, the substitution of hydrogen by methyl at Y atom of the $Y(CH_3)_3$ Lewis bases seems to have an important effect upon the stability of the complexes. It is important to realize that the bond strength of a donor–acceptor complex is not only determined by the nature of the Lewis acid but that is also depends strongly on the Lewis base. It is not possible to obtain an absolute scale for the Lewis acidity or Lewis basicity, the strength of the two entities can only be given with a specific counter species as reference.

Table 3 lists the computed complexation energies for the $X_3AlY(CH_3)_3$ (X = H, F, and Cl; Y = N, P, and As) donor–acceptor complexes and the charge transfer from $Y(CH_3)_3$ Lewis bases to AlX_3 Lewis acids (Q_t). The complexation energies are calculated as the difference between the energies of the complexes and the respective donor–acceptor moieties. The estimation of the basis set superposition error (BSSE) for all the structures presented here was performed by the full counterpoise method at the MP2/6–311++G(df,p) level. These results are also presented in Table 3.

Table 3. E_c (Complexation Energies), BSSE, E_{c+BSSE}, E_c(MP2(full)) (kcal/mol), and Charge Transfer Q_t (*e*)

Complex	E_c ^{a,b}	BSSE ^{c}	E_{c+BSSE} ^{a,b}	E_c(MP2(full)) ^{d}	Q_t
$H_3AlN(CH_3)_3$	–33.12 (–27.28)	4.30	–28.81 (–23.84)	–33.64	0.15
$H_3AlP(CH_3)_3$	–25.99 (–14.63)	3.52	–22.47 (–11.33)	–26.49	0.34
$H_3AlAs(CH_3)_3$	–20.33 (–10.63)	2.30	–18.02 (–9.12)	–21.41	0.33
$F_3AlN(CH_3)_3$	–47.75 (–40.79)	7.20	–40.55 (–35.80)	–48.72	0.11
$F_3AlP(CH_3)_3$	–36.56 (–22.33)	5.47	–31.09 (–17.52)	–37.37	0.31
$F_3AlAs(CH_3)_3$	–29.81 (–17.30)	4.01	–25.80 (–14.11)	–31.36	0.30
$Cl_3AlN(CH_3)_3$	–48.33 (–37.90)	11.35	–36.98 (–31.72)	–49.32	0.14
$Cl_3AlP(CH_3)_3$	–39.06 (–20.51)	8.72	–30.34 (–14.71)	–39.91	0.39
$Cl_3AlAs((CH_3)_3$	–31.55 (–15.63)	6.84	–24.71 (–12.15)	–33.24	0.40

[a] $E_{comp} = E(X_3AlY(CH_3)_3) – [E(X_3Al) + E(Y(CH_3)_3)]$ (X = H, F, and Cl; Y = N, P, and As).
[b] The values in parenthesis correspond to the non methylated complexes.
[c] Calculated using the counterpoise method.
[d] MP2(Full)/6–311++G(df,p)//MP2/6–311++G(df,p) level.

The BSSE goes from 2.30 kcal/mol for the $H_3AlAs(CH_3)_3$ complex to 11.35 kcal/mol for the $Cl_3AlN(CH_3)_3$ complex. Table 3 shows that BSSE is higher and must be taken into account. The calculated complexation energies E_c of the halogen alane Lewis acids with $Y(CH_3)_3$ (Y = N, P, and As) Lewis bases show the trend $N(CH_3)_3 > P(CH_3)_3 > As(CH_3)_3$ at the MP2/6–311++G(df,p) + BSSE corrections level of theory. In order to evaluate the effect of the inner electron, we have also calculated the complexation energies at the MP2(full)/6–311++G(df,p)//MP2/6–311++G(df,p) level of theory. These results are also reported in Table 3. We can see form Table 3 that the trends are similar to those obtained at the MP2/6–311++G(df,p) level of theory. Nevertheless, the $N(CH_3)_3$ complexes with AlX_3 (X = H, F, and Cl) Lewis acids are calculated to be more strongly bound than the respective $P(CH_3)_3$ and $As(CH_3)_3$ complexes. In addition, the energetic results show that the stability decreases when going from nitrogen to arsenic for all complexes. Indeed, the complexation energies of $H_3AlN(CH_3)_3$, $H_3AlP(CH_3)_3$, and $H_3AlAs(CH_3)_3$ are –28.81, –22.47, and –18.02 kcal/mol, respectively, while the complexation energies of $F_3AlN(CH_3)_3$, $F_3AlP(CH_3)_3$, and $F_3AlAs(CH_3)_3$ are –40.55, –31.09, and –25.80 kcal/mol, respectively, and the complexation energies of $Cl_3AlN(CH_3)_3$, $Cl_3AlP(CH_3)_3$, and $Cl_3AlAs(CH_3)_3$ are –36.98, –30.34, and –24.71 kcal/mol, respectively. On the other hand, one can observe that the complexation energy of the alane complexes show the trend $AlCl_3 \geq AlF_3 > AlH_3$ at the MP2/6–311++G(df,p) level and $AlF_3 \geq AlCl_3 > AlH_3$ at the MP2/6–311++G(df,p) + BSSE level of theory. The inversion of the trend is due to the higher BSSE correction for the chlorine complexes. Indeed, Figure 2 shows nicely that $N(CH_3)_3$ leads always to the more stable complex among the Lewis bases.

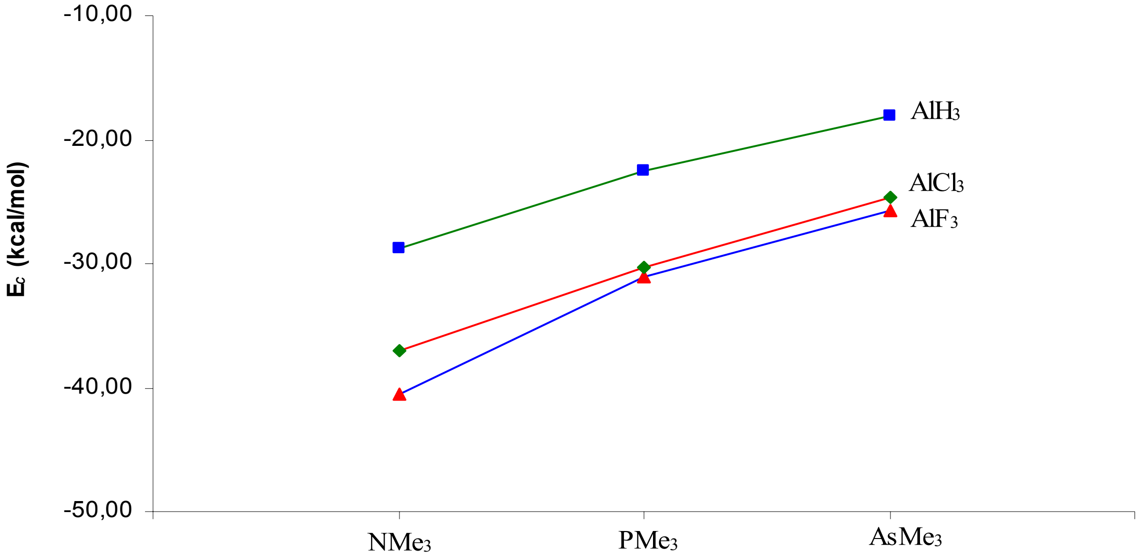


Figure 2. Trend of the calculated complexation energies (including BSSE correction) of the $X_3AlY(CH_3)_3$ (X = H, F, and Cl; Y = N, P, and As) complexes.

In order to evaluate the effect of methyl substitution, we have also computed the complexation energies of the X_3AlYH_3 donor–acceptor complexes, at the same MP2/6–311++(df,p) level of theory The estimation of the basis set superposition error (BSSE) was also performed by the full counterpoise method at the MP2/6–311++G(df,p) level. These results are also presented in Table 3. The substitution of hydrogen by methyl on central atom (Y) of the donor fragment, the complexation energy increases. This effect is more important with the phosphorus complexes. Indeed, the substitution of hydrogen by methyl stabilizes the complex by ~5, ~11, and ~9 kcal/mol for $H_3AlN(CH_3)_3$, $H_3AlP(CH_3)_3$, and $H_3AlAs(CH_3)_3$ complexes, respectively. A similar trend is observed with the AlF_3. The stabilization effect is more slightly important upon methyl substitution of the Cl_3AlXH_3 (X = N, P, and As) complexes. On the other hand, Figure 3 shows nicely that the methyl substitution effect is more important with the phosphorus complexes.

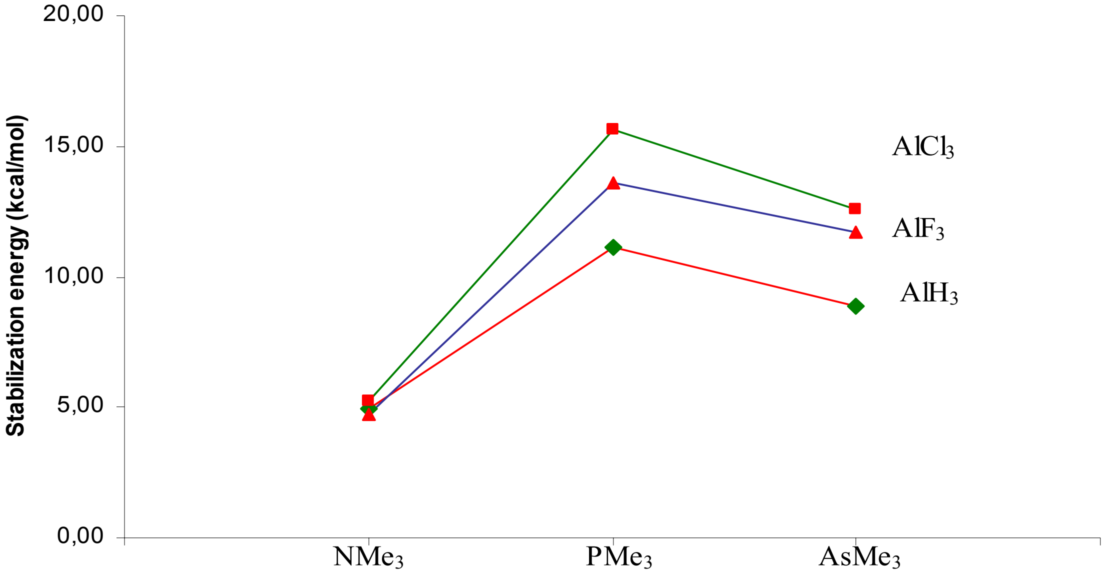


Figure 3. Trend of the calculated stabilization energies upon methyl substitution.

The calculated NBO charge transfer listed in Table 3 show that the $X_3AlN(CH_3)_3$ complexes have a lower charge transfer from $N(CH_3)_3$ to AlX_3 acceptor moieties. On the other hand, the NBO calculated net charges show that the nitrogen partial charge of $N(CH_3)_3$ moiety (–0.61 *e*) is negative. The net partial charges of the phosphorus and the arsenic atoms are positive 0.83 and 0.90 *e*, respectively. This is contrary to the scale of stability between the $N(CH_3)_3$ complexes and their homologous $P(CH_3)_3$ and $As(CH_3)_3$ ones. In fact, the charge transfer from $N(CH_3)_3$ to AlX_3 (X = H, F, and Cl) is lower than that from $P(CH_3)_3$ and $As(CH_3)_3$, while the complexation energies of $X_3AlN(CH_3)_3$ complexes are higher than that for $X_3AlP(CH_3)_3$ and $X_3AlAs(CH_3)_3$ complexes (see Table 3). Moreover, the $F_3AlN(CH_3)_3$ complex is the most stable ($E_{c + BSSE} = -40.55$ kcal/mol) and it show only a lower charge transfer (0.11 *e*), whereas the less stable complex is $H_3AlAs(CH_3)_3$ ($E_{c + BSSE} = -18.02$ kcal/mol) and is shows a charge transfer of 0.33 *e*. Hence, one can see that from the NBO results it follows that there is no correlation between charge transfer and the calculated complexation energy of $X_3AlY(CH_3)_3$ (X = H, F, and Cl; Y = N, P, and As) donor–acceptor complexes.

4 CONCLUSIONS

Ab initio calculations have been carried out to study the interaction in $X_3AlY(CH_3)_3$ (X = H, F, Cl; Y = N, P, and As) donor–acceptor complexes. We have shown that the stability decreases when descending in the corresponding column of the ligand central donor atom. The energetic results show that the substitution of hydrogen by methyl increases the stability of the complexes investigated in this work. Upon complexation, the structural parameters of $X_3AlY(CH_3)_3$ (Y = P and As) complexes show an irregular shortening of the Y–C bonds. The analysis of the electronic structure based on natural bond orbitals (NBO) partitioning scheme shows that this shortening was related to the increasing of the ‘s’ character and Wiberg bond index in these bonds. It also indicates that there is no correlation between the charge transfer and the stability of the complex.

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