

# Basicity and Nucleophilicity Effect in Charge Transfer of ALH3-Base Adducts

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## Research Article

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**BASICITY AND NUCLEOPHILICITY EFFECT IN CHARGE TRANSFER OF ALH<sub>3</sub>-  
BASE ADDUCTS**

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## Abstract

This study permits to explore the interactions involved in Lewis acid ( $\text{AlH}_3$ ) and Lewis bases:  $\text{CO}$ ;  $\text{H}_2\text{O}$ ;  $\text{NH}_3$ ;  $\text{PH}_3$ ;  $\text{PCl}_3$ ;  $\text{H}_2\text{S}$ ;  $\text{CN}^-$ ;  $\text{OH}^-$ ;  $\text{O}_2^{2-}$ ;  $\text{F}^-$ ;  $\text{N}(\text{CH}_3)_3$ ;  $\text{N}_2$ ;  $\text{N}_2\text{H}_4$ ;  $\text{N}_2\text{H}_2$ ; pyridine; aniline. By means of DFT theory calculations with B3LYP functional using 6-31G(d,p) basis set and in order to check the effects of both the donor and the acceptor in the establishment of the different adducts we focused mainly on the calculation of the energetic gap  $\Delta E_{\text{HOMO-LUMO}}$ , Gibbs energies  $\Delta G$ , the angle ( $\theta$ ) in  $\text{AlH}_3$ -Base and the interaction energy values  $E_{\text{int}}$ . The several parameters of the reactivity (electrophilicity index ( $\omega$ ), nucleophilicity ( $N$ ), chemical potential ( $\mu$ ), hardness ( $\eta$ ) and polarizability ( $\alpha$ ) are also calculated to defined the weak interaction as well as to distinguish between the nucleophilicity and basicity of the different Lewis basis.

Our results showed that the electronic charge transfer is estimated to be important in the systems where the interaction is established between Al and anionic bases, and the electron donor power is predictable for  $\text{O}^{2-}$ ,  $\text{F}^-$ ,  $\text{OH}^-$  and  $\text{CN}^-$ . The pseudo-tetrahedral adduct arrangements depend on the parameter geometries (bond length interaction and  $\theta$  angle) and Gibbs energies  $\Delta G$  characterizing the main stability.

**Keywords:** Lewis acid-base interaction, adduct dtability, DFT, nucleophilicity, charge transfer.

## INTRODUCTION

Lewis acid-base interaction adducts include a partially formed dative bond that provide several new and intriguing viewpoints on molecular structure and bonding [1]. The adducts are characterized by the interaction between the electron rich sites of basis and featuring electron hole of acids, and thus, are in the considerable interest for understanding chemical bonding [2,3]. This concept is the broadest, and it may be used to classify a large range of events as acid-base reactions. It is therefore not surprising that discussions of Lewis acidity and basicity appears in almost every textbook of general, organic and inorganic chemistry [4]. Much effort has gone into developing a fundamental measure for estimating Lewis acidity in solids [5,6], which has proven to be problematic. The majority of the frequent metric is the strength of a basic molecules binding to an acidic site. The most used explanation for this interaction is represented by the electron density in a frontier orbital, resulting from a modest change in the overall number of electrons [7].

In addition, a number of theoretical efforts have been made to provide qualitative and quantitative insights into these basic notions. From a theoretical standpoint, it has been noted that density functional theory (DFT) offers an effective framework for the creation and investigation of a chemical reactivity theory [8,9]. A rising number of gas-phase and theoretical research molecular structure [10] is not an unchanging aspect of a molecule in this context, but rather demonstrates a remarkable phase dependency [11].

In this study, and following to our previous work [12] we will explore more detail about the interactions established between molecules or between molecules and ions. So, in the investigation below, our interest is the Lewis acid–base interactions which is realized among  $\text{AlH}_3$  and a series of neutral and anionic bases ( $\text{CO}$ ;  $\text{H}_2\text{O}$ ;  $\text{NH}_3$ ;  $\text{PH}_3$ ;  $\text{PCl}_3$ ;  $\text{H}_2\text{S}$ ;  $\text{CN}^-$ ;  $\text{OH}^-$ ;  $\text{O}_2^{2-}$ ;  $\text{F}^-$ ;  $\text{N}(\text{CH}_3)_3$ ;  $\text{N}_2$ ;  $\text{N}_2\text{H}_4$ ;  $\text{N}_2\text{H}_2$ ; pyridine; aniline) are stems from the fact that they are

quite strong and pseudo-tetrahedral in the coordination chemistry [13]. We have examined the nature of the interaction, the strength bonding, and the stability of adducts. Moreover, the concepts of HOMO and LUMO orbitals in describing electron-donor (Lewis-Base) and electron-acceptor (Lewis-Acid) interactions are introduced to estimate and to classify the bases according to their nucleophilicity [14]. Thus, the dipolar moment is used as an important property for donor-acceptor adducts as a fundamental measure of charge distribution.

The big request that occurs when a Lewis acid-base reaction takes place, and leads to the creation of a covalent bond between the acid and the base [15, 16] according to the literature: This bond does not necessarily comprise the entire electronic doublet originating from the base, but rather a fraction of it, which may be clarified using various charge transfer methods [17].

This study aims to present quantitative answers:

- How do the Lewis donor-acceptor interactions influence the occupancies of the involved bonds?
- This interaction causes complete transfer of the electronic doublets or just a partially dative bond?
- What factors influence the quality of the resulting bond and the adducts stability?

## **THEORY BACKGROUND**

### **HSAB (Hard and Soft Acids and Bases) PRINCIPLE**

Pearson established the HSAB hypothesis, or acid-base concept, in 1963 [18], and it is commonly used in chemistry to describe compound stability and reaction rate. The concept was introduced in relation to the behavior of Lewis acids (A) and bases (B).



Since the complex molecules or ions, A: B, were considered to be formed from an acceptor electrons A and an electron donor B, since the acid-base complex, A: B, can be an organic molecule, an inorganic molecule or a complex ion.

The stability of A:B It is the result of the acid-base interaction between the two parts. Any insight into the properties of A and B that leads to the formation of a forte binding, would be very helpful. It was well known that there is no one order of acidic force, or of basic strength, which would be vigorous in any case. The "force" here is used in the sense of connection strength formation: that is, a strong acid and a strong base will form the same strong bond.

Based on this classification, Pearson [19] formulated his HSAB principle (hard and soft acids and bases main HSAB) as follows: "Hard acids prefer to react with hard bases and soft acids prefer to react with soft bases".

### **IONIZATION POTENTIAL I [20]**

Pearson et al showed that the Mulliken electronegativity ( $\chi$ ) and the hardness ( $\eta$ ), analogous to the first- and second-derivatives of energy with respect to number of electrons, respectively, can be used to measure Lewis acidity with more accuracy. Applying a finite

difference approximation for the first derivative and three-point finite difference approximation for the second derivative leads to operational definitions in terms of ionization potential (I) and electron affinity (A) as follows:

The ionization potential and electron affinity can be replaced by the HOMO and LUMO energies, respectively, using Koopmans' theorem [21] within a Hartree-Fock scheme yielding

$$I = -E_{HOMO} \dots \dots \dots (2)$$

$$A = -E_{LUMO} \dots \dots \dots (3)$$

Parr and co-workers [22] interpreted that chemical potential ( $\mu$ ) could be written as the partial derivative of the system's energy with respect to the number of electrons at a fixed external potential  $v(\vec{r})$ :

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{v(\vec{r})} = \frac{1}{2}(I + A) \dots \dots \dots (4)$$

$$\eta = \left(\frac{\partial^2 E}{\partial N^2}\right)_{v(\vec{r})} = \frac{1}{2}(I - A) \dots \dots \dots (5)$$

$$\eta = \frac{1}{2}(I - A) = \frac{1}{2}(E_{HOMO} - E_{LUMO}) \dots \dots \dots (6)$$

$$\mu = -\frac{1}{2}(I + A) = -\frac{1}{2}(E_{HOMO} + E_{LUMO}) \dots \dots \dots (7)$$

$$\chi = \frac{1}{2}(I + A) = \frac{1}{2}(E_{HOMO} + E_{LUMO}) \dots \dots \dots (8)$$

Parr and al [22] have introduced the global electrophilicity index ( $\omega$ ) as a measure of energy lowering due to maximal electron flow between a donor and an acceptor in terms of the chemical potential and the hardness as:

$$\omega = \frac{\mu^2}{2\eta} \dots \dots \dots (9)$$

Hardness [23,24] is one of the most significant global reactivity descriptors. Hardness is described as one of the key global reactivity descriptors, and has the definition in equation (7) The vertical ionization energy and electron affinity, respectively, are I and A. The reciprocal of hardness is softness (S) [25] which is defined as

$$S = \frac{1}{2\eta} \dots \dots \dots (10)$$

In 2007, Gázquez introduced the concepts of the electroaccepting,  $\omega^+$ , and electrodonating,  $\omega^-$ , powers as [26]:

$$\omega^+ = \frac{A^2}{2(I - A)} \dots \dots \dots (11)$$

$$\omega^- = \frac{I^2}{2(I - A)} \dots \dots \dots (12)$$

where  $\omega^+$  represents a measure of the propensity of a given system to accept electron density, while  $\omega^-$  represents the propensity of this system to donate electron density.

In 2008, we proposed an empirical (relative) nucleophilicity N index for closed-shell organic molecules based on the HOMO energies,  $E_{\text{HOMO}}$ , obtained within the Kohn-Sham scheme as an approach to the gas phase, and defined as [27]:

$$N = E_{\text{HOMO}}(\text{Nucleophile}) - E_{\text{HOMO}}(\text{TCE}) \dots \dots \dots (13)$$

The nucleophilicity  $N$  index is referred to tetracyanoethylene (TCE), which is the most electrophilic neutral species, the expected least nucleophilic neutral species. This choice allowed convenient handling of a nucleophilicity scale of positive values. An analysis of a series of common nucleophilic species participating in polar organic reactions allowed a further classification of organic molecules as strong nucleophiles with  $N > 3.0$  eV, moderate nucleophiles with  $2.0 \leq N \leq 3.0$  eV and marginal nucleophiles with  $N < 2.0$  eV [28]

In our calculations we have found the  $E_{\text{HOMO}}(\text{TCE}) = -9.121$  eV at B3LYP/6-31G(d,p) level.

Besides, the maximum number of electrons  $\Delta N_{\text{max}}$  that an electrophile can acquire is given by the expression [29]

$$\Delta N_{\text{max}} = -\frac{\mu}{\eta} \dots \dots \dots (14)$$

The maximum charge that each species may accept from the environment which is measured by  $\Delta N_{\text{max}}$ , is almost parallel to the variation in electrophilicity for whole series of Lewis acid-base adducts. Since the nucleophilicity index obtained as  $\frac{1}{\omega^-}$  was below, we can define the nucleophilicity as  $N'' = \frac{10}{\omega^-}$

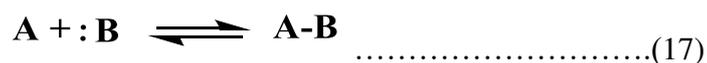
Following methods [30] were adopted for the present study.

$$N' = \frac{1}{\omega^-} \text{ where } \omega = \frac{\mu^2}{2\eta} \dots \dots \dots (15)$$

$$N'' = \frac{1}{\omega^-} \text{ where } \omega^- = \frac{I^2}{2(I - A)} \dots \dots \dots (16)$$

## CHARGE TRANSFER ANALYSIS ( $\Delta N$ )

Acids are electron-pair acceptors and bases are electron-pair donor, according to the original Lewis definition (1923 [31], 1938 [32]). The creation of a complex (or adduct, or coordination compound) A–B reaction (17) is the crucial reaction between a Lewis acid A and a Lewis base B.



Lewis acids and basis are electron-pair acceptors and electron-pair donors, respectively, according to the Lewis theory of acid-base reactions. As a result, a Lewis base can transfer two electrons to a Lewis acid, in generally resulting in a product with a coordinate covalent bond.

This suggests that Lewis acid-base is a complicated interaction that is influenced by the entire system rather than just the isolated acids and bases.

When two systems, B and A, are combined, electrons move from the lower  $\chi$  to the higher  $\chi$  until the chemical potentials are equal. For generalized acid-base reactions, the fractional number of electrons transferred.

A + :B  $\rightarrow$  A:B, (up to first order) is provided by

$$\Delta N = \frac{(\chi_A - \chi_B)}{2(\eta_A - \eta_B)} \dots\dots\dots(18)$$

The global interactions between AlH<sub>3</sub> and the selected bases of systems have been determined using the parameter ΔN, which represents the fractional number of electrons, transferred from a system A to a system B. Charge transfer data are presented in Table-5-. Generally, electron flows from less electronegative system to more electronegative and this fact along with the definition of ΔN clearly shows that charge transfer values are negative for AlH<sub>3</sub>-CO and AlH<sub>3</sub>-N<sub>2</sub> showing them as electron donors, and for the remains of the adducts ΔN is positive representing them as electron acceptors.

The maximum charge transfer is estimated in the interaction between AlH<sub>3</sub> and O<sup>-2</sup> (2.28), and between AlH<sub>3</sub> and H<sub>2</sub>S with (1.54) then between AlH<sub>3</sub> and F<sup>-</sup> (1.34). The smallest donate charge is among AlH<sub>3</sub> and PCl<sub>3</sub> with (0.00015). Whereas, the energy that following this charge transfer eq.(19) indicates that AlH<sub>3</sub>-PCl<sub>3</sub> is repaired by the great value of energy (-3.97 x 10<sup>-8</sup>).

The reduction in energy caused by this electron transfer from a greater chemical potential (base) to a lower chemical potential (acid) is provided by [33].

$$\Delta E = \frac{(\chi_A - \chi_B)^2}{4(\eta_A + \eta_B)} \dots \dots \dots (19)$$

## COMPUTATIONAL DETAILS

Geometry optimizations and frequency calculations of all the molecules and adducts were carried out using density functional theory along with three-parameter hybrid model (DFT/B3LYP) [34-36] in conjunction with 6-31G(d,p) basis function. All quantum chemical calculations were performed using the Gaussian 09 program [37]. All the optimized geometries have no negative vibrational modes showing that all structures are minima on the potential energy surface.

## RESULTS AND DISCUSSION

### STRUCTURE OF $\text{AlH}_3$ LEWIS ACID

**Fig.1.** (a) The planar geometry of  $\text{AlH}_3$ ; (b) the electrostatic potential map for molecular surface (c) the molecular orbital LUMO of  $\text{AlH}_3$

$\text{AlH}_3$  or alane, is a sterically and electronically unsaturated moiety that reacts readily with a range of Lewis-basis, leading to 1 : 1 and 1 : 2 adducts which are respectively four- or five-coordinate at the Al centre [38-40]. The four-coordinate 1 : 1 adducts of alane ( $\text{AlH}_3\text{-B}$ ) generally adopt a pseudo-tetrahedral configuration at the Aluminium centre [41].

In our results of geometry optimization presented in Fig.1.; the planar geometry of the Lewis acid  $\text{AlH}_3$  appears with  $\text{Al-H} = 1.59 \text{ \AA}$  and the angle  $\text{H-Al-H}$  is equal to  $120^\circ$ . The map of the electrostatic potential (EP) for the molecular surface of Lewis acid is also illustrated and tends to be between  $\pm 7.113 e^{-2}$ . The blue region of EP relates to positive charge of the aluminium center, nevertheless the electron-rich sites congregate in the green hue area of EP and belongs to the negative charge of hydrogens. The LUMO orbital is clearly located on the aluminium center that present the electronic hole. The aim calculated parameters of  $\text{AlH}_3$  are presented in Table 1.

The interactions of  $\text{AlH}_3$  with a variety of Lewis-basis suggests that the aluminium center has direct contact with the various atoms X of the Lewis-basis (Fig.2.) and that leads to a pseudo-tetrahedral configuration adducts.

**Fig.2.** (1) tetrahedral ( $\text{AlH}_4$ )<sup>-</sup> and (2) pseudo-tetrahedral  $\text{AlH}_3\text{---Base}$  geometries

**Table 1.** energy and essential parameters of AlH<sub>3</sub> Lewis acid

## NEUTRAL AND ANIONIC LEWIS BASES

**Fig.3.**Structure and Mulliken charge of considered Lewis bases.

**Table 2.**les principaux paramètres des bases de Lewis

**Table 3.** Nucleophilicity index  $N$  (eV) of chosen bases

The nucleophilicity  $N$  estimated theoretically and listed in Table 3. for some anionic and neutral bases (Fig.3.). Obtained results shown that the more nucleophilic base is O<sup>-2</sup> (26.801eV) which is in accordance with the values of the global electrophilicity index  $\omega$  (36.634) and the electrodonating  $\omega^-$  (6.444). Therefore, the classification of the bases according to their nucleophilicity is: O<sup>-2</sup>, F<sup>-</sup>, OH<sup>-</sup>, CN<sup>-</sup>, N<sub>2</sub>H<sub>4</sub>, N(CH<sub>3</sub>)<sub>3</sub>, Aniline, N<sub>2</sub>H<sub>2</sub>, NH<sub>3</sub>=N<sub>2</sub>, Pyridine, H<sub>2</sub>S, H<sub>2</sub>O, PH<sub>3</sub>, C=O, PCl<sub>3</sub>. whereas, their classification according to the electrodonating  $\omega^-$  does not follow the same order: O<sup>-2</sup>, N<sub>2</sub>, PCl<sub>3</sub>, C=O, N<sub>2</sub>H<sub>2</sub>, Pyridine, H<sub>2</sub>S, PH<sub>3</sub>, Aniline, H<sub>2</sub>O, NH<sub>3</sub>, N(CH<sub>3</sub>)<sub>3</sub>, N<sub>2</sub>H<sub>4</sub>, OH<sup>-</sup>, F<sup>-</sup>, CN<sup>-</sup>.

The low ionization energy  $I$  shows that the molecule is highly reactive. according to Table 2. the increasing order of potential ionization is (-17.682eV O<sup>-2</sup>) < (-4.572eV for F<sup>-</sup>) < (-4.365eV for OH<sup>-</sup>) < (-0.506eV for CN<sup>-</sup>) < (4.433eV for N<sub>2</sub>H<sub>4</sub>) < ( 5.635eV for N(CH<sub>3</sub>)<sub>3</sub>) < (6.544eV

for aniline) < ( 6.560eV N<sub>2</sub>H<sub>2</sub>) < (6.609eV for NH<sub>3</sub>) < (6.873eV for pyridine) < (7.124eV for H<sub>2</sub>S) < ( 7.485eV for PH<sub>3</sub>) < (7.943eV for H<sub>2</sub>O) < (8.231eV for PCl<sub>3</sub>) < (10.107eV for C=O) < (11.629eV for N<sub>2</sub>).

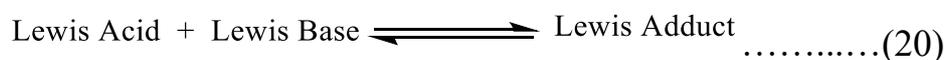
The value of  $\Delta N_{max}$  determines the maximum charge that each basis may accept from the environment. Negative values of  $\Delta N_{max}$  indicate the maximum charge that the bases can give. Table 3. shows the most electronic charge donation is from O<sup>-2</sup> with  $\Delta N_{max}$  equal to (-2.458), then OH<sup>-</sup> can gives (-2.257), F<sup>-</sup> input a (-1.287) and the least contribution is by CN<sup>-</sup> (-1.111).

### NUCLEOPHILICITY CHARACTER IN CHOSEN BASES

According to the Lewis definition, Lewis bases have high electron density centers, while Lewis acids have low electron density centers. The electron pair provided by the base is utilized to establish a new sigma bond to the electron deficient site in the acid. The conversion of the lone pair between the base and the empty orbital of the acid into a covalent bond is known as a Lewis acid-base interaction. Eq. (20).

Nucleophilicity is not a measurement of lone pair reactivity, that is basicity which measures a thermodynamic quality (end-result stability levels of reactants and products). While nucleophilicity measures a kinetic quality (the speed of giving the electron pair). According to this concept, and to clarify the Lewis AlH<sub>3</sub>-base interactions, we have drawn the energy levels of the HOMO orbitals for each interacting base (Fig.4.) that acts as electron pair donors.

O<sup>-2</sup> presents the highest HOMO energy (17.68eV) compared to the other bases which leads to the best estimate of nucleophilicity and therefore, we can classify all bases with the order of nucleophilicity: O<sup>-2</sup> > F<sup>-</sup> > OH<sup>-</sup> > CN<sup>-</sup> > N<sub>2</sub>H<sub>4</sub> > N(CH<sub>3</sub>)<sub>3</sub> > aniline > N<sub>2</sub>H<sub>2</sub> > NH<sub>3</sub> > pyridine.



$$\Delta G = G_{\text{Adduct}} - G_{\text{Lewis Acid}} - G_{\text{Lewis Base}} \dots \dots \dots (21)$$

$$\Delta H = H_{\text{Adduct}} - H_{\text{Lewis Acid}} - H_{\text{Lewis Base}} \dots \dots \dots (22)$$

## MEASUREMENT OF LEWIS BASICITY

The term "basicity" refers to a thermodynamic concept. The location of an equilibrium is determined by the respective stabilities of the entities included in the two members of the acido-basic eq. (20) (associated): this may be expressed using the formula  $\Delta G = -RT \log K$ , where  $\Delta G$  is the free standard variation of enthalpy of the reaction.

According to the glossary of terms used in physical organic chemistry published by the International Union of Pure and Applied Chemistry [42], Lewis basicity is defined as follows: The thermodynamic tendency of a substance to act as a Lewis base. Comparative measures of this property are provided by the equilibrium constants for Lewis adduct formation for a series of Lewis bases with a common reference Lewis acid.

A number of groups (Drago [43,44], Gutmann [45,46], Maria and Gal [47] Arnett et al [48] have proposed measuring Lewis (Bronsted) basicity from the negative enthalpies of the complexation (protonation) reactions (20). In order to follow the IUPAC definition of basicity [49], We suggest reserving basicity measurements for Gibbs energies  $\Delta G$  of adduct formation (protonation) and referring to the relevant enthalpies as 'enthalpy of basicity' [50].

## Interaction Lewis acid-base

in the Lewis acid-base interaction, the Lewis acid intervenes through its orbital LUMO to receive the electron doublet. On the other hand, the Lewis base intervenes by orbital HOMO which includes an electronic doublet to give it.

In the Lewis acid-base interaction diagram, the energy gap  $\Delta E_1$  between  $LUMO_{ALH_3}$  and  $HOMO_{O^{2-}}$  is estimated at 19.618 eV. Depending on the results obtained from the deviations, this value appears to be the highest, which reflects the difficulty of  $O^{2-}$  in giving their electronic doublet to the aluminum center. The HOMO of  $O^{2-}$  is more energetic than the LUMO of  $ALH_3$ , allowing laborious interaction to place the non-binding doublets of  $O^{2-}$  in a lower energy orbital. The energy gap (Fig.4.) indicates that the electron donor power which is estimated in the following increasing order:  $CN^- < N_2H_4 < N(CH_3)_3 < N_2H_2 < aniline < NH_3 < Pyridine < H_2S < PH_3 < H_2O < PCl_3 < OH^- < F^- < CO < N_2 < O^{2-}$ .

The above classification makes it possible to give the order of the nucleophilicity of the cited bases, therefore  $CN^-$  appears as the most nucleophilic while  $O^{2-}$  is the least nucleophilic.

**Fig.4.** Estimation of the nucleophilicity via the energetic gap  $\Delta E$  between  $HOMO_{Basis}$  and  $LUMO_{AlH_3}$

## STABILITY AND CHARGE TRANSFER OF ADDUCTS

**THE PARAMETERS STABILITY:**  $\Delta E_{inter}$ ,  $\Delta E_{HOMO-LUMO}$  and the angle  $\theta$

### INTERACTION ENERGY $\Delta E_{inter}$

The system of the two interacting molecules, A and B, is treated as a supermolecule or as a complex and their interaction energy,  $\Delta E$ , is the energy of the supermolecule or of the complex minus the energies of the isolated molecules [51]:

$$\Delta E_{inter} = EAB - (EA + EB) \dots \dots \dots (24)$$

The lower interaction energy is according to the more stable supermolecule or complex. In our case, the interaction energy for anionic adducts appears as a lower in the case of  $\text{AlH}_3\text{---O}_2^{-2}$  (-20.524 au), while for neutral adducts

### FRONTIER MOLECULAR ORBITALS (FMO)

Molecular orbitals and their properties such as energy are useful for chemists in frontier electron density for predicting the most reactive systems [20] and also explains several types of reactions in conjugated systems. FMO analysis is widely employed to explain the optical and electronic properties of organic compounds [52].

The DFT method predicts that the HOMO – LUMO energy gap of obtained adducts which is found to be very low in the case of  $\text{AlH}_3\text{-N}_2\text{H}_2$  (3.78eV) and it leads to less stability (high chemical reactivity) of the complex and it is more polarizable (43.133 a.u).

### The angle $\theta$ and Al-O bond

In regular tetrahedral geometry ( $\text{AlX}_4^-$ ) the angle  $\theta$  is estimated at  $109.64^\circ$ . When the base interacts with  $\text{AlH}_3$  a pseudo-tetrahedral geometry ( $\text{AlH}_3\text{B}$ ) is appeared and the angle  $\theta$  value may reflect a good parameter stability. On the other hand, Al-O bond length is between 1.64 to 1.69 in many compounds with four-coordinate aluminium [53]. The value that is most similar to regular  $\theta$  is indicated in  $\text{AlH}_3\text{-F}^-$  adduct ( $109.52^\circ$ ) and the distance Al-F is equal to 1.14Å.

Whereas, in  $\text{AlH}_3\text{-O}_2^{-2}$  adduct a best bond length establishes among Al and  $\text{O}_2^{-2}$  (1.69Å) and  $\theta$  is to  $118.62^\circ$ . in addition, the values of  $\theta$  in  $\text{AlH}_3\text{-CN}^-$  and  $\text{AlH}_3\text{-OH}^-$  are  $106.98^\circ$  and  $111.47^\circ$  respectively. Their bond lengths, Al-CN<sup>-</sup> (1.94Å) and Al-OH<sup>-</sup> (1.80Å), seems to be

the optimal distances Table 4. Except for AlH<sub>3</sub>-pyridine and AlH<sub>3</sub>-aniline, the remaining structures present an angle  $\theta$  less than 100°.

Optimized structures of all adducts with Mullikan atomic charge and the main bond lengths are shown in Fig.5. AlH<sub>3</sub>---base bond length (Å) and the corresponding IR stretching frequency ( $cm^{-1}$ ), dipolar moment and induced dipolar moment in (Deby), the fractional charge transfer ( $\Delta N$ ), the interaction energy  $E_{int}$ , the polarizability ( $\alpha$ ), the enthalpy  $\Delta H_{adduct}$  in (Kcal/mol) and the free Gibbs energies  $\Delta G_{adduct}$  in (Kcal/mol) calculated at the same level and at T = 298.15 °K are listed in Table 5. The order of stability in the considered adducts is AlH<sub>3</sub>-O<sup>-2</sup> > AlH<sub>3</sub>-PCl<sub>3</sub> > AlH<sub>3</sub>-CN<sup>-</sup> > AlH<sub>3</sub>-H<sub>2</sub>S > AlH<sub>3</sub>-OH<sup>-</sup> > AlH<sub>3</sub>-PH<sub>3</sub> > AlH<sub>3</sub>-N<sub>2</sub>H<sub>2</sub> > AlH<sub>3</sub>-NH<sub>3</sub> > AlH<sub>3</sub>-aniline > AlH<sub>3</sub>-N<sub>2</sub>H<sub>4</sub> > AlH<sub>3</sub>-F<sup>-</sup> > AlH<sub>3</sub>-pyridine > AlH<sub>3</sub>-H<sub>2</sub>O > AlH<sub>3</sub>-CO > AlH<sub>3</sub>-N<sub>2</sub>.

**Table 4.** energetic parameters of ALH<sub>3</sub>... base adducts

**Table 5.** Dipolar Moment ( $\mu$ ), Polarizability ( $\alpha$ ),  $\Delta G_{Adduct}$ ,  $\Delta H_{Adduct}$ ,  $\Delta\mu_{ind}$ ,  $\Delta N$  and  $\Delta E_{CT}$ .

**Fig.5.** Optimized adducts at B3LYP/6-31G(d,p) level.

Table 6. shows the frontier orbitals (HOMO and LUMO plots) and the estimation of the energetic gap  $\Delta E_{HOMO-LUMO}$ . Besides, the electrostatic surface potential map is also displayed for all adducts.

By comparing the  $\Delta E_{HOMO-LUMO}$  values of different adducts, and as a result, we may categorize the structures as follows:  $AlH_3-N(CH_3)_3 > AlH_3-PH_3 > AlH_3-F > AlH_3-N_2H_4 > AlH_3-H_2S > AlH_3-NH_3 > AlH_3-OH^- > AlH_3-H_2O > AlH_3-aniline > AlH_3-CO > AlH_3-N_2 > AlH_3-CN^- > AlH_3-PCl_3 > AlH_3-O^{2-} > AlH_3-pyridine > AlH_3-N_2H_2$ . The highest value is associated to  $AlH_3-N(CH_3)_3$  with (7.65eV) and then helps to understand difficult of charge transfer.

The electrostatic potential of the molecule (MEP) is still a helpful guide determining a molecules reactivity toward positively or negatively charged structures. The MEP is usually displayed by projecting its values onto a surface that reflects the boundaries of the molecules.

In the electrostatic potential map Table 6. The total density depicts the localization of charges surrounding the atoms; it should be noticed that the richness of electrons is concentrated in the red and yellow color regions, the blue region of EP relates to the positive charge.

The largest interval of electron density has been found for  $AlH_3-H_2O$  structure, and it tends to be between  $\mp 9.548 e^{-2}$ . While the restraint interval of electron density characterizes  $AlH_3-N_2H_2$  adduct and it tends toward  $\mp 0.101 e^0$ .

**Table 6.** The HOMO and LUMO plots,  $\Delta E_{HOMO-LUMO}$ (eV) and the electrostatic surface potential map (ESP).

## CHARGE TRANSFER IN LEWIS ACID-BASE ADDUCTS

### INDUCED DIPOLAR MOMENT

Dipolar moment [54] is an important property for donor-acceptor complexes as a fundamental measure of charge distribution in gas phase [55] or in solution [56].

In this work, we present the calculated values of dipolar moment, at B3LYP/6-31G(d,p) level of theory, of sixteen bases and Lewis acid-bases adducts. The obtained results are used to examine the relationship between the dipolar moment induced by complexation and the length bond of donor-acceptor system. The quantity of charge transfer can be used to understand the Lewis acid-base adducts bond.

Generally, the induced dipolar moment of an adduct  $AB$  ( $\mu_{AB}$ ) obtained from the dipolar moment of Lewis acid  $A$  ( $\mu_A$ ) and Lewis base  $B$  ( $\mu_B$ ) can be given by the variation [57]:

$$\Delta\mu_{\text{ind}} = \mu_{AB} - \mu_A - \mu_B \dots \dots \dots (25)$$

The Mulliken charge analysis and the Natural bond orbital (NBO) are important tools for studying intermolecular and intramolecular interactions, as well as a good starting point for investigating net charge transference in molecular systems.

### **The NBO theory**

NBO analysis has already proved to be an effective tool for the chemical interpretation of hyperconjugative interactions and electron density transfer from the filled lone-pair electron [58]. The orbital natural binding (NBO) method of Weinhold et al [59] provides a suitable scheme for the analysis of Lewis acid-base interactions [60] because it emphasizes the computation of the delocalization of the electron density in vacant orbitals.

An interesting example is provided by the NBO analysis of the water dimer  $\text{H}_2\text{O} \dots \text{H}-\text{O}-\text{H}$ , where the left and right molecules act like the Lewis base and Lewis acid, respectively. Interaction energy is broken down into charge transfer (CT) and no charge transfer (NCT) as follows:

$$\Delta E = \Delta E_{NCT} + \Delta E_{CT} \dots \dots \dots (25)$$

For each donor NBO(*i*) and acceptor NBO(*j*), the stabilization energy ( $E_2$ ) associated with the delocalization  $i \rightarrow j$  is given by [61]

$$E_2 = \Delta E_{ij} = q_i \left( \frac{F_{(i,j)}^2}{\epsilon_i - \epsilon_j} \right) \dots \dots \dots (26)$$

In our case, the significant interaction in the calculate adduct structures are listed in Table 7.

**Table 7.** Donor and acceptor NBO and energy details of AlH<sub>3</sub>—Bases adducts

In AlH<sub>3</sub>-CN<sup>-</sup>, the occupancy of Al-N bond is (1.986) which is mainly obtained from lone pair of N atom. The intramolecular interactions LP(C1)→σ\*<sub>N2-Al</sub> and σ<sub>N2-Al</sub>→σ\*<sub>Al-H6</sub> with stabilization energies (1.99kcal/mol) and (12.18 kcal/mol) respectively. Similarly, intramolecular interaction from σ<sub>N2-Al</sub> to σ\*<sub>Al-H6</sub> leading to the stabilization energy of (15.80kca/mole).

The strong intramolecular interactions appear in AlH<sub>3</sub>-O<sup>-2</sup> where the occupancy of Al-O is (1.9343). σ<sub>Al-O5</sub> →σ\*<sub>Al-H4</sub> ; σ<sub>Al-O5</sub> →σ\*<sub>Al-H2</sub> and σ<sub>Al-O5</sub> →σ\*<sub>Al-H3</sub> going to lead stabilization energies 21.02 ; 15.74 ; 15.80 kcal /mol) separately.

In the major cases, the partial charge transfer from the formed Al-base goes to the non-bonding σ\*<sub>Al-H</sub> orbital. While in AlH<sub>3</sub>-N<sub>2</sub> the lone pair nitrogen atom LP(N6), has a high occupation number (1.9837) with p-character (~67%), donates an electron to the antibonding σ\*<sub>Al-N5</sub> with 4.25 kcal/mol energy of interaction.

It is noted that in AlH<sub>3</sub>-Pyridine and AlH<sub>3</sub>-aniline, lone pair Lp(N5) of nitrogen atom with p-character (74.95%) has an occupied number of (1.8054) and (1.8096) respectively. Their interactions LP(N5)→LP\*(Al) are with considerably higher stabilization energies (69.58 and

58.38 kcal/mol). The adduct systems are stabilized as a result of the intramolecular charge transfer.  $\pi \rightarrow \pi^*$  interactions occur between the bonding  $\pi_{\text{N5-C10}}$  and antibonding orbitals  $\pi^*_{\text{C6-C7}}$  as well as the bonding  $\pi_{\text{C2-C3}}$  and antibonding orbitals  $\pi^*_{\text{C1-C6}}$ , with a strong stabilization energy 91.09 and 244.39 kcal/mol respectively.

In comparison,  $\sigma \rightarrow \sigma^*$  interactions have the lowest delocalization energy compared with  $\pi \rightarrow \pi^*$  interactions. As a result, the  $\sigma$  bonds have higher electron density occupancy than the  $\pi$  bonds.

## CONCLUSION

In this investigation, using at DFT/B3LYP/6-31G(d,p) level of theory, we have described the concept of the partial dative bond which can be established in the Lewis acid-base interaction. Besides, this work provides detailed insights into the electronic structure properties using the conceptual DFT to determine the major factors that control the formation of this bond and the stability of the produced adducts.

The charge transfer plays a crucial role in describing dative bond formation,  $\Delta N$ ,  $\Delta N_{\text{max}}$  and the energy following the charge transfer  $\Delta E$ , the electrodonating  $\omega^-$ , and the potential ionization permit to quantify and classify  $\text{O}^{2-}$  as the best nucleophilic system.

The interactions that take place revealed to be capable of explaining the activity of the lone pairs to participate in the new bonding that appear in the Lewis acid-base interaction. Calculating of energetic gap between HOMO of the bases and the LUMO of  $\text{AlH}_3$  indicate that  $\text{CN}^-$  have the power lone pair donation by the lowest  $\Delta E = 2.442\text{eV}$ .

Calculated Gibbs energies allowed us to describing the stable obtained adducts give us the following order:  $\text{AlH}_3\text{-O}^{2-} > \text{AlH}_3\text{-PCl}_3 > \text{AlH}_3\text{-CN}^- > \text{AlH}_3\text{-H}_2\text{S} > \text{AlH}_3\text{-OH}^- > \text{AlH}_3\text{-PH}_3 >$

$\text{AlH}_3\text{-N}_2\text{H}_2 > \text{AlH}_3\text{-NH}_3 > \text{AlH}_3\text{-aniline} > \text{AlH}_3\text{-N}_2\text{H}_4 > \text{AlH}_3\text{-F}^- > \text{AlH}_3\text{-pyridine} > \text{AlH}_3\text{-H}_2\text{O}$   
>  $\text{AlH}_3\text{-CO} > \text{AlH}_3\text{-N}_2$ .

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### **-Conflicts of interest/Competing interests**

“The authors declare that they have no conflict of interest”

### **-Availability of data and material**

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**-Code availability:** MESRS: N° 59 du 27/04/2010

### **Authors' contributions**

All authors participated in the realization of this work. Dr. Aichi Mouhamed Made theoretical calculations, Dr. Hafied Meriem Made theoretical results, the discussion and the focus of results. Dr. Dibi Ammar: Revised the manuscript and elucidated all the manuscript.

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# Figures

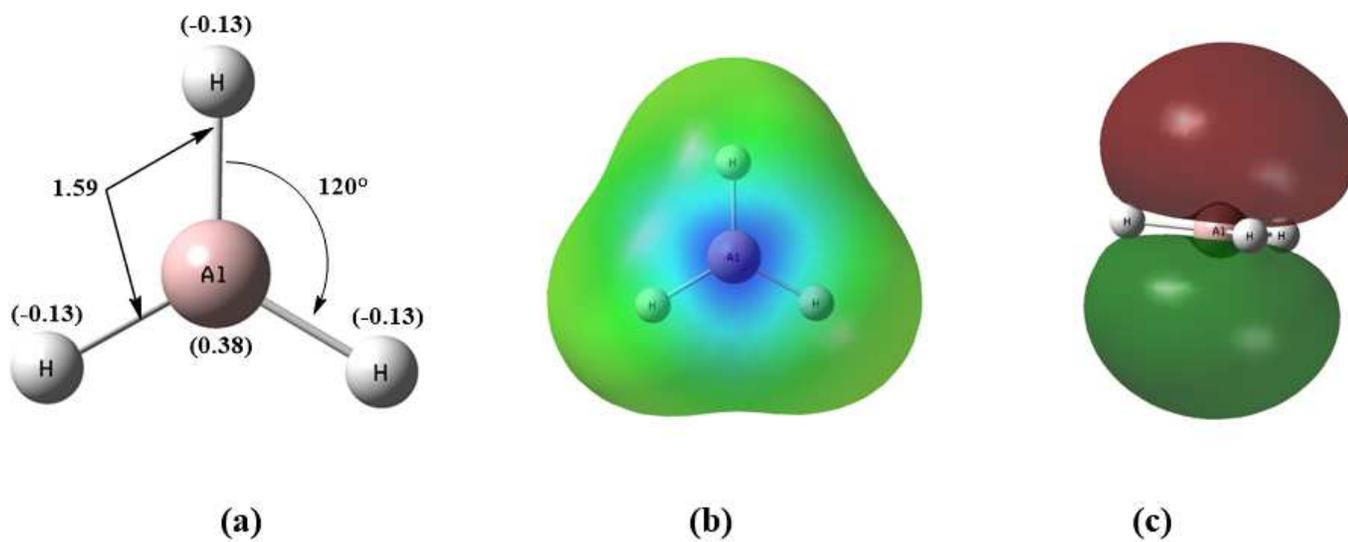


Figure 1

(a) The planar geometry of  $\text{AlH}_3$ ; (b) the electrostatic potential map for molecular surface (c) the molecular orbital LUMO of  $\text{AlH}_3$

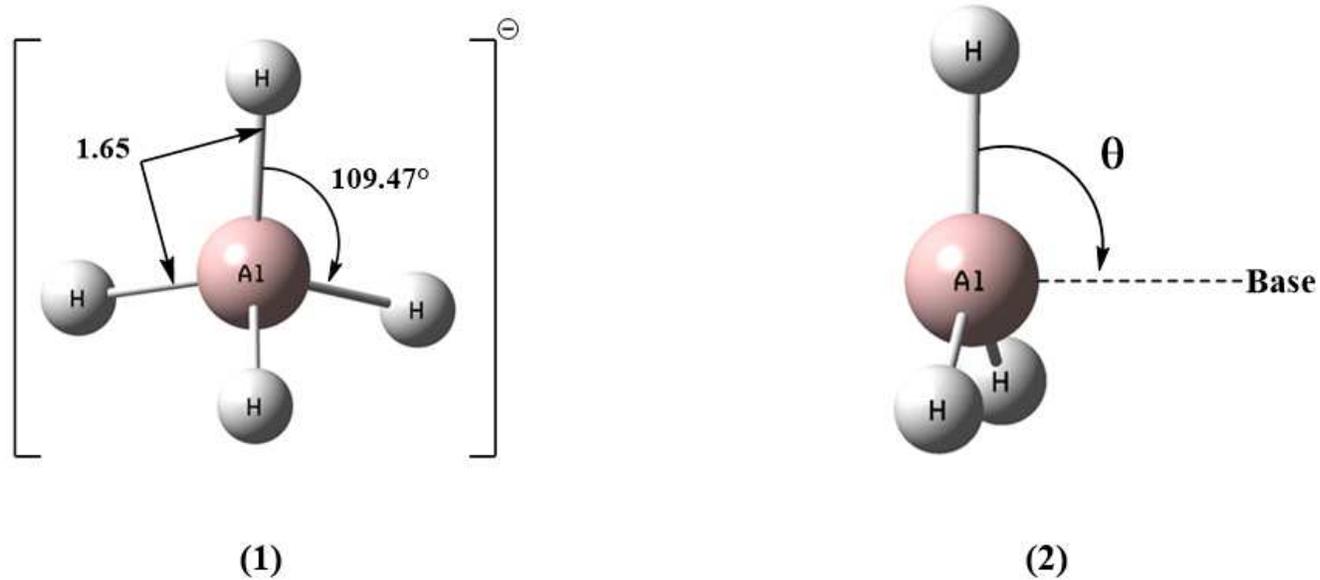
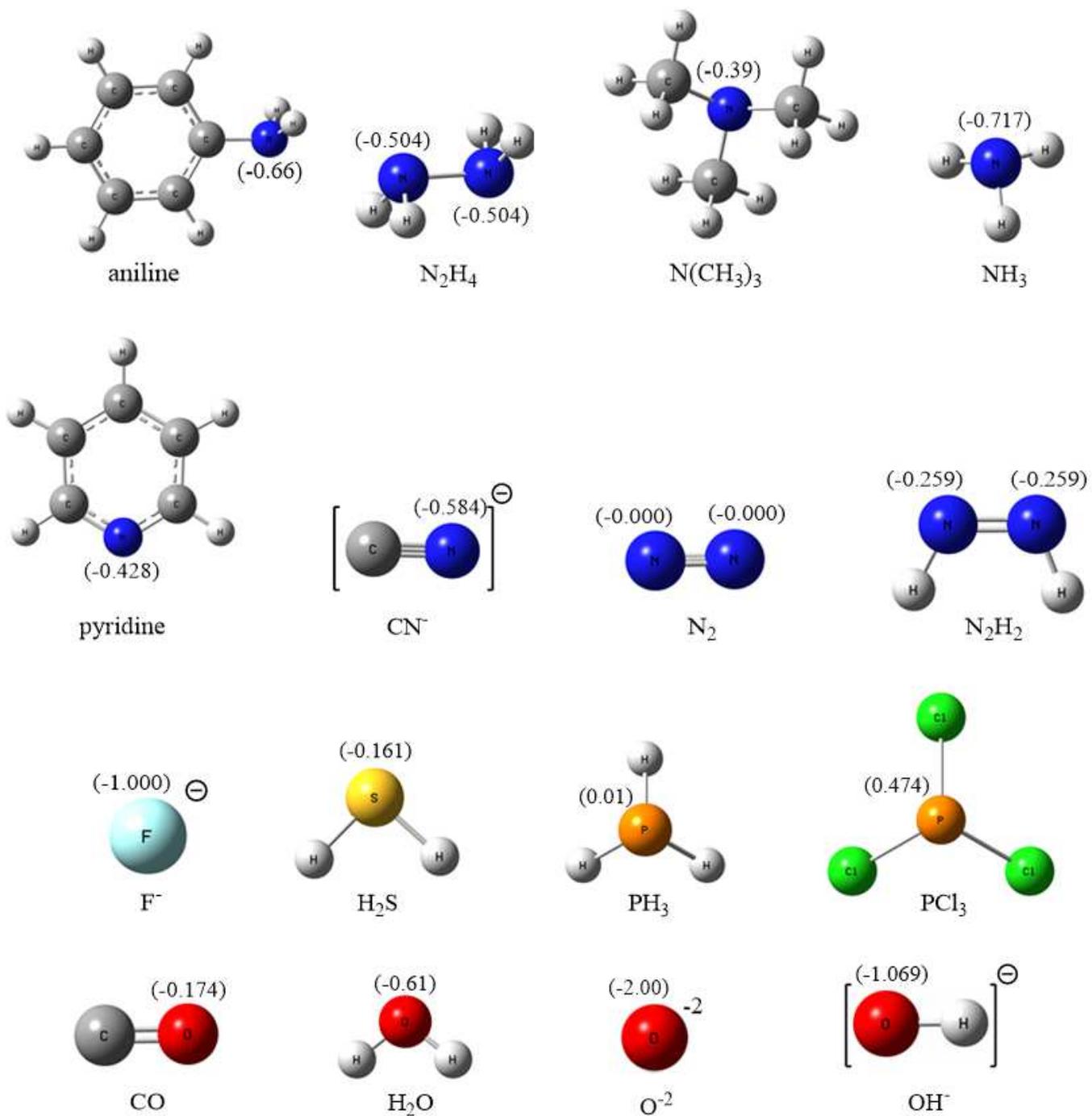


Figure 2

(1) tetrahedral  $(\text{AlH}_4)^-$  and (2) pseudo-tetrahedral  $\text{AlH}_3$ -Base geometries



**Figure 3**

Structure and Mulliken charge of considered Lewis bases.

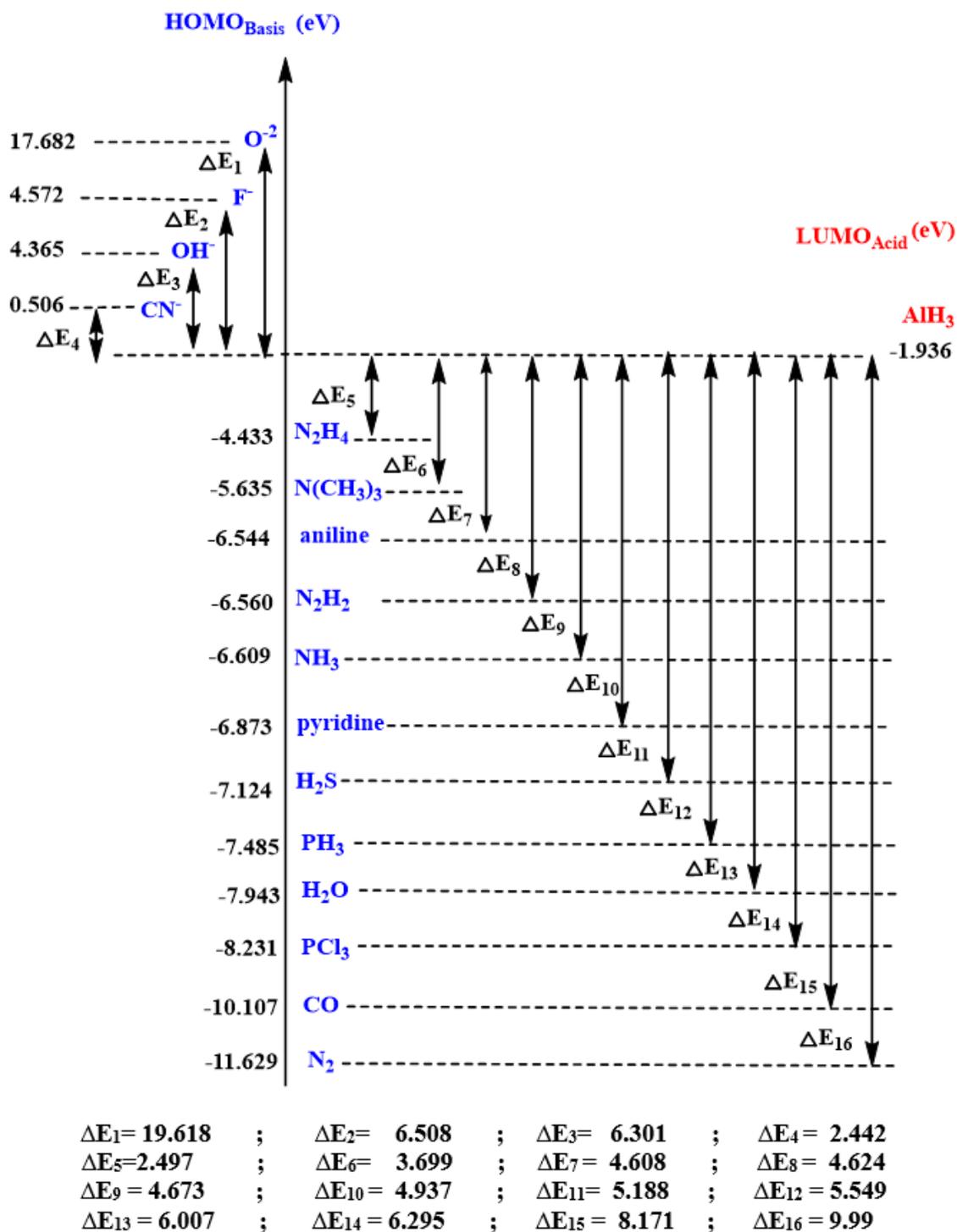
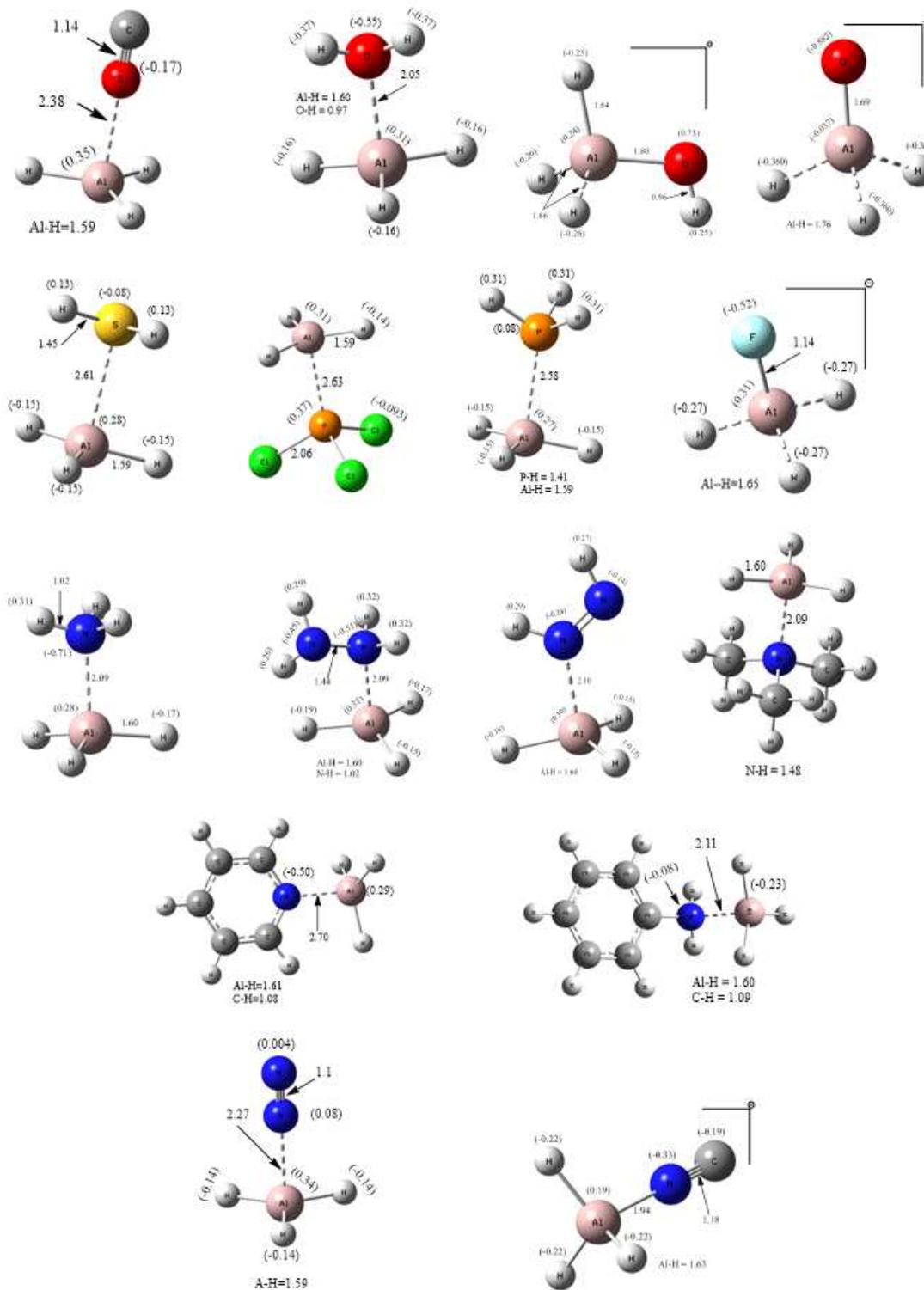


Figure 4

Estimation of the nucleophilicity via the energetic gap  $\Delta E$  between HOMO<sub>Basis</sub> and LUMO<sub>AlH<sub>3</sub></sub>



**Figure 5**

Optimized adducts at B3LYP/6-31G(d,p) level.

## Supplementary Files

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