

# Density Functional Theory and Semi-empirical Investigations of Amino Tetrahydrofuran Molecules

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**Abstract** This document gives formatting instructions for authors preparing papers for publication in the journal. Authors are encouraged to prepare manuscripts directly using this template. This template demonstrates format requirements for the Journal.

**Keywords:** tetrahydrofuran molecules, density functional theory, semi-empirical investigations

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## 1. Introduction

Density functional theory (DFT) is a quantum mechanical theory used in physics and chemistry to investigate the electronic structure (principally the ground state) of many-body systems, in particular atoms, molecules, and the condensed phases. With this theory, the properties of a many-electron system can be determined by using functional, i.e. functions of another function, which in this case is the spatially dependent electron density. Hence the term density functional theory comes from the use of functional of the electron density. DFT is among the most popular and versatile methods available in condensed-matter physics, computational physics, and computational chemistry [1,2].

The *ab initio* methods, especially when including electron correlation, are computationally intensive. This limits their ability to handle large sized molecules. Semi-empirical methods provide a means for obtaining computational results for large sized molecules and inorganic molecules including transition state elements [3,4].

Semi-empirical calculations are set up with the same general structure as a HF calculation in that they have a Hamiltonian and a wave function. Within this framework, certain pieces of information are approximated or completely omitted. Usually, the core electrons are not included in the calculation and only a minimal basis set is used. Also, some of the two-electron integrals are omitted. In order to correct for the errors introduced by omitting part of the calculation, the method is parameterized. Parameters to estimate the omitted values are obtained by fitting the results to experimental data or *ab initio* calculations. Often, these parameters replace some of the integrals that are excluded [3,4].

Tetrahydrofuran (THF) is an organic compound with the formula  $(\text{CH}_2)_4\text{O}$ . It is a colorless, water-miscible

organic liquid with low viscosity at standard temperature and pressure. The compound is heterocyclic. As one of the most polar ethers with a wide liquid range, it is a useful solvent. Its main use is as a precursor to polymers. THF has an odor similar to its chemical cousin, diethyl ether, but is a much less potent anesthetic than diethyl ether.

About two hundred thousand tonnes of tetrahydrofuran are produced annually. [5] The most widely used industrial process involves the acid-catalyzed dehydration of 1,4-butanediol, akin to the production of diethyl ether from ethanol. The butanediol is derived from condensation of acetylene with formaldehyde followed by hydrogenation. [6] Du Pont developed a process for producing THF by oxidizing n-butane to crude maleic anhydride followed by catalytic hydrogenation. [7] A third major industrial route entails hydroformylation of allyl alcohol followed by hydrogenation to the butanediol.

THF can also be synthesized by catalytic hydrogenation of furan. [8,9] Where furan is derived from pentose, this method can involve renewable resources. Nevertheless, this route is not widely practiced.

It can be polymerized by strong acids to give a linear polymer called poly (tetramethylene ether) glycol (PTMEG), CAS Registry Number [25190-06-1], also known as PTMO, polytetramethylene oxide. The primary use of this polymer is to make elastomeric polyurethane fibers like Spandex [10].

THF is also a starting material for the preparation of tetrahydrothiophene using hydrogen sulfide over a heterogenous acid catalyst [11].

The other main application of THF is as an industrial solvent for PVC and in varnishes. [6] It is an aprotic solvent with a dielectric constant of 7.6. It is a moderately polar solvent and can dissolve a wide range of nonpolar and polar chemical compounds. [12] THF is water-miscible, and can form solid clathrate hydrate structures with water at low temperatures [13].

Although a minor application, THF is a popular solvent in the laboratory when a moderately higher-boiling

etheral solvent is required and its water miscibility is not an issue. The oxygen center of ethers can coordinate to Lewis acids such as  $\text{Li}^+$ ,  $\text{Mg}^{2+}$ , and boranes, forming adducts. Hence, like diethyl ether, THF can be used in hydroboration reactions to synthesize primary alcohols, and as a solvent for organometallic compounds such as organolithium and Grignard reagents. [14] Although similar to diethyl ether, THF is a stronger base. [15] Thus, while diethyl ether remains the solvent of choice for some reactions (e.g., Grignard reactions), THF fills that role in many others where strong coordination is desirable, and the precise properties of ethereal solvents such as these (alone and in mixtures and at various temperatures) allows for fine-tuning modern chemical reactions.

## 2. Theoretical Methods and Computational Details

The molecular properties for the new molecules is computed under the Becke three parameters with Lee-Yang-Parr functional [B3LYP] level with large 6-31G basis set.

The mathematical equations were use in the calculations included:

$$IP = E(+)-E(n) \quad (1)$$

Where (*IP*): is the Ionization potential for an molecule is the amount of energy required to remove an electron from an isolated atom or molecule, and expressed as the energy difference between the positive charged energy  $E(+)$  and the neutral energy  $E(n)$ .

Electron affinity (EA) of an molecule is the energy change when an electron is added to the neutral atom to form a negative ion, and expressed as the energy

difference between the neutral energy  $E(n)$  and the negative charged energy  $E(-)$ , as in the following relation:

$$EA = E(n) - E(-) \quad (2)$$

From equations (1) and (2), we can calculate the electronic chemical potential ( $\kappa$ ), the hardness ( $\mu$ ) and the softness [16]:

$$k = \frac{IP + EA}{2} \quad (3)$$

$$\mu = \frac{IP - EA}{2} \quad (4)$$

$$s = \frac{1}{2\mu} \quad (5)$$

$$w = \frac{k^2}{2\mu} \quad (6)$$

Where

$\kappa$ : is the electronic chemical potential. It is that the quantity that measures the escaping tendency of electrons from species in its ground state.

$\mu$ : is the hardness and define that the measurement of molecule resistance to the change or deformation in molecular orbital.

$s$ : is the softness of the molecules [17].

$\omega$ : is the electrophilicity which species that stabilize upon receiving an additional amount of electronic charge from the environment.

Energy gap ( $E_{\text{gap}}$ ): is the different between the lowest unoccupied molecular orbital and highest occupied molecular orbital according to the Koopmans theorem [18].

$$E_{\text{gap}} = LUMO_{\text{energy}} - HOMO_{\text{energy}} \quad (7)$$

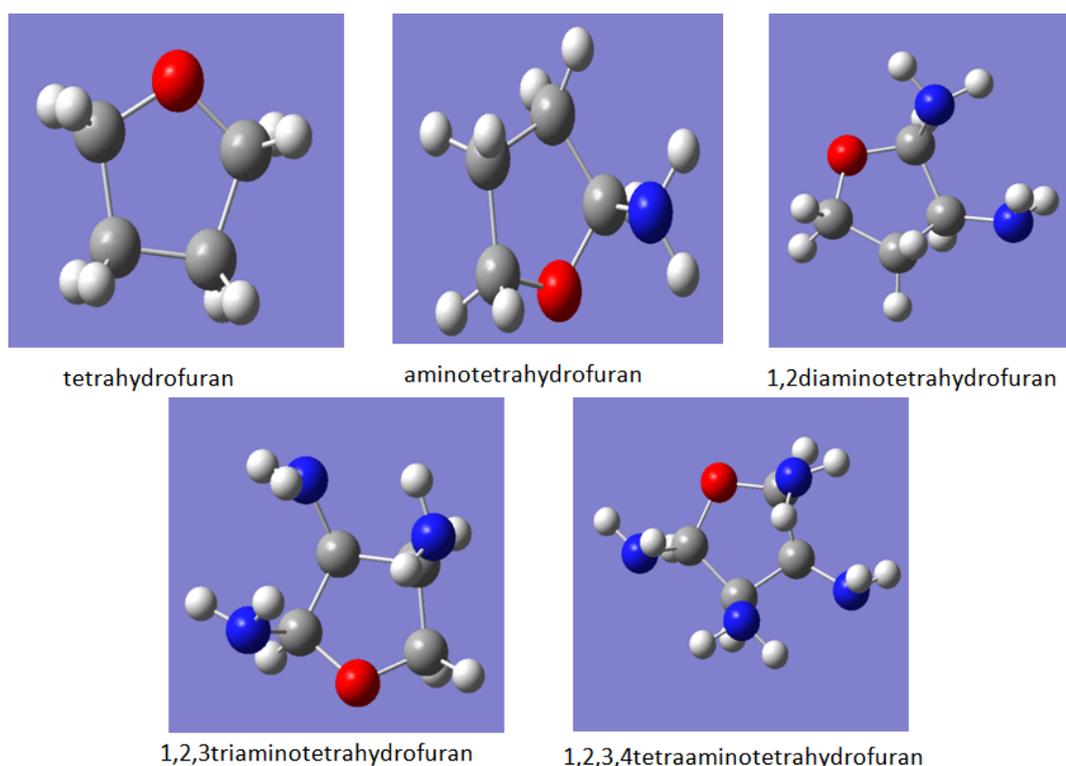


Figure 1. shows the optimized structure of studied molecules

### 3. Results and Discussion

Density functional theory and semi-empirical used in this research. For study the electronic properties and electronic structure of saturated molecules. However, a large time required for employing this level and this time increases with increasing the radical used to describe the studied molecules, where characterizes by it is not economic time.

The electronic structure and electronic properties of the tetrahydrofuran were studied and then addition the (NH<sub>2</sub>) radical in different position and different number to the

tetrahydrofuran. The optimization of geometry of each molecule is shows in Figure 1.

Figure 2 shows the Relation between total energy and No. of NH<sub>2</sub> groups. It is obvious from the figure that the total energy for all mentioned molecules is less than the total energy of tetrahydrofuran molecule, and it is decreased with increase of NH<sub>2</sub> groups number added to tetrahydrofuran molecule, The calculated total energy for the molecules by AM1 method is far away from these by B3LYP/6-31G\*\* method, as it was illustrated earlier that the semi-empirical methods are not adequate to calculate the total energy.

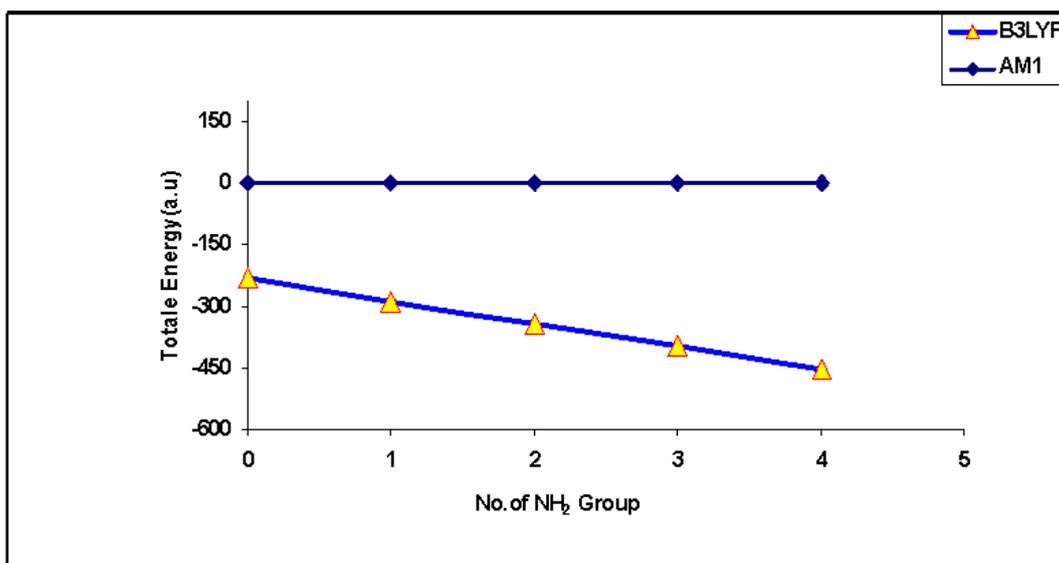


Figure 2. Relation between total energy and No. of NH<sub>2</sub> groups

Figure 3 shows the relation between the ionization potential and the number of NH<sub>2</sub> groups, it is clear from this figure that the ionization potential for the amino tetrahydrofuran molecule groups is less than the ionization potential for tetrahydrofuran molecule, but the 1,2,3,4 tetrahydrofuran molecule has the least, this mean that this

molecule needs a small energy to become cation comparing with other molecules. Generally, the curve goes toward low IP but a small upper hope in number of groups No. = 3, this is a global property and it is not coming from frontier molecular orbital.

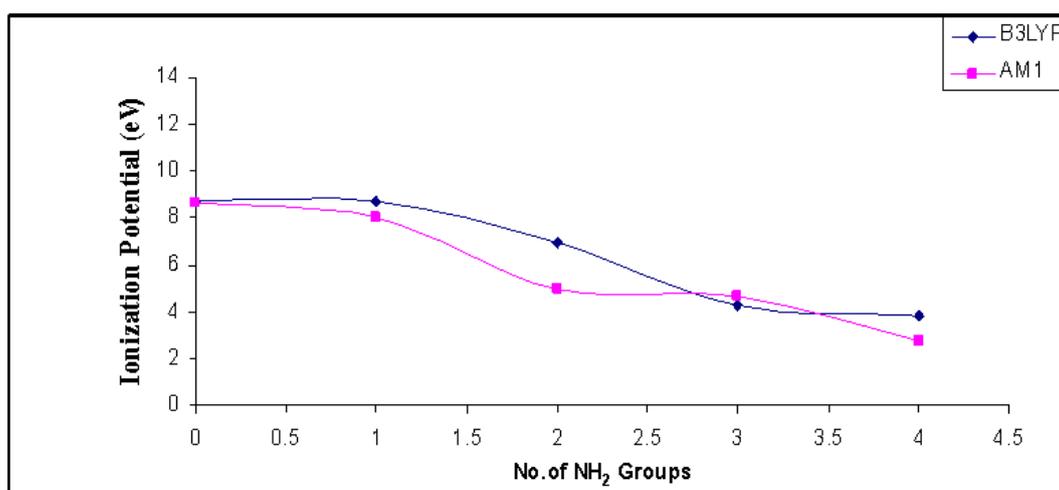


Figure 3. Relation between ionization potential and No. of NH<sub>2</sub> groups

Figure 4 shows the influence of groups number on the electron affinity (EA) of studied compounds. It is clear from this figure that the electron affinity which calculated by (AM1) has negative values for all compounds, this may be an indication to a resistance for receiving an electron,

this figure indicates that electron affinity for the amino tetrahydrofuran groups molecules is more than the electron affinity for tetrahydrofuran molecule, but the electron affinity computed by B3LYP/6-31G\*\* is larger than the electron affinity computed by AM1.

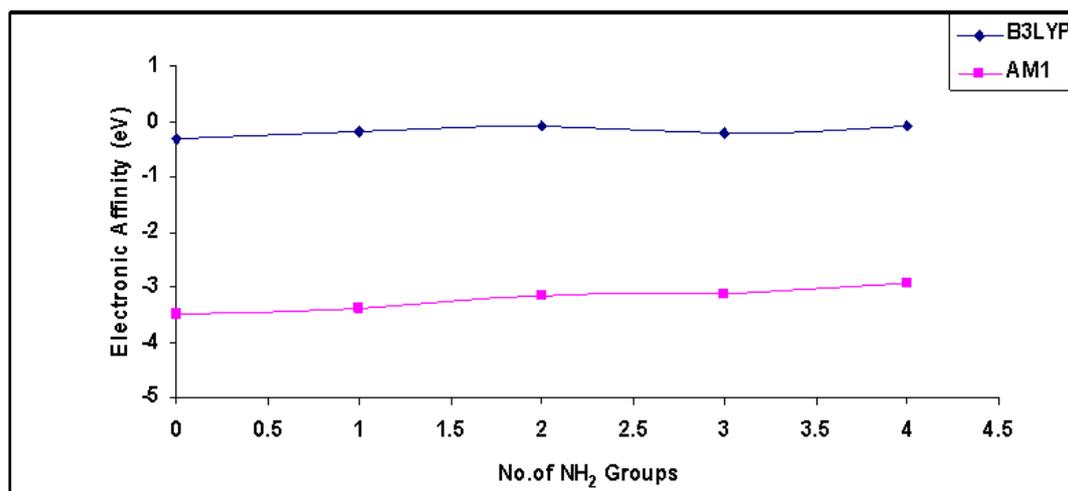


Figure 4. Relation between electron affinity and No. of NH<sub>2</sub> groups

Figure 5 shows the relation between the chemical potential and the number of NH<sub>2</sub> groups, it is obvious from this figure that all four molecules have a chemical

potential less than that for tetrahydrofuran molecule alone, that means the electrons in these molecules have a large escaping tendency.

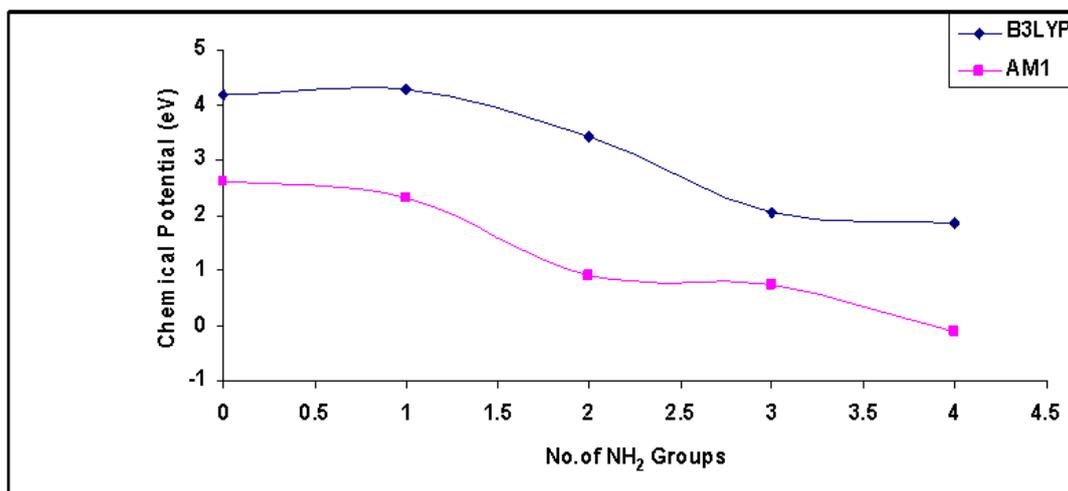


Figure 5. Relation between chemical potential and No. of NH<sub>2</sub> groups

Figure 6 shows the relation between the hardness and the number of NH<sub>2</sub> groups, it is clear from this figure that the hardness of all molecules is smaller than

tetrahydrofuran molecule for both B3LYP/6-31G\*\* and AM1 methods.

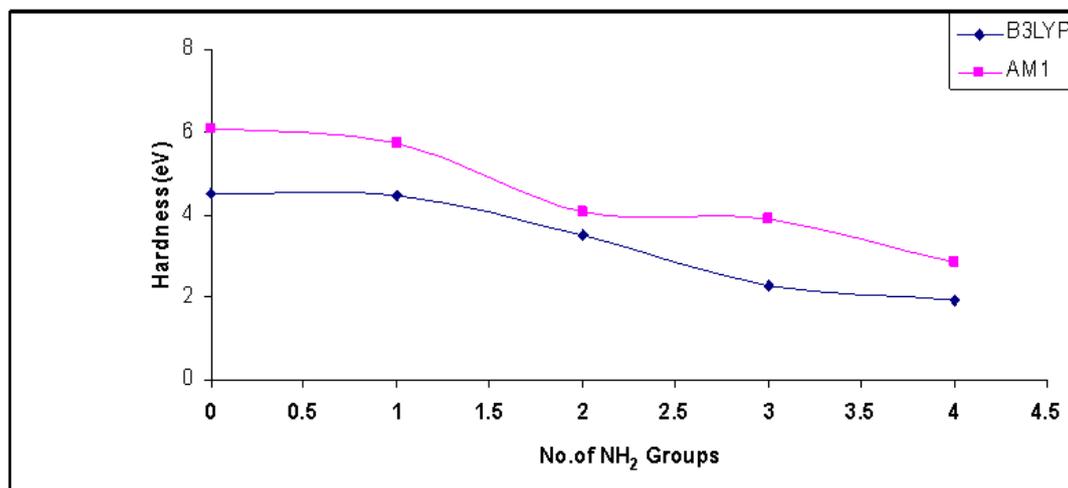


Figure 6. Relation between hardness and No. of NH<sub>2</sub> groups

Figure 7 show the relation between total dipole moment and the number of NH<sub>2</sub> groups calculated by B3LYP/6-

31G\*\* and AM1 methods. The result has been found convergence with little difference.

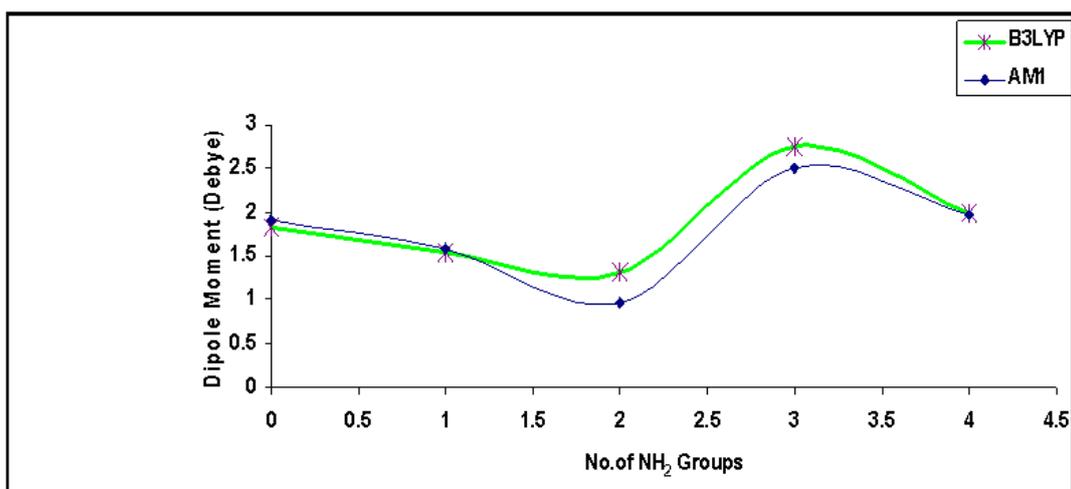


Figure 7. Relation between total dipole moment and No. of NH<sub>2</sub> groups

Figure 8 show the relation between softness in (a.u) unite and the number of NH<sub>2</sub> groups calculated by B3LYP/6-31G\*\* and AM1 methods. It is obvious from this figure that all four molecules have a softness greater

than that for tetrahydrofuran molecule alone, that means the electrons in these molecules have a small escaping tendency.

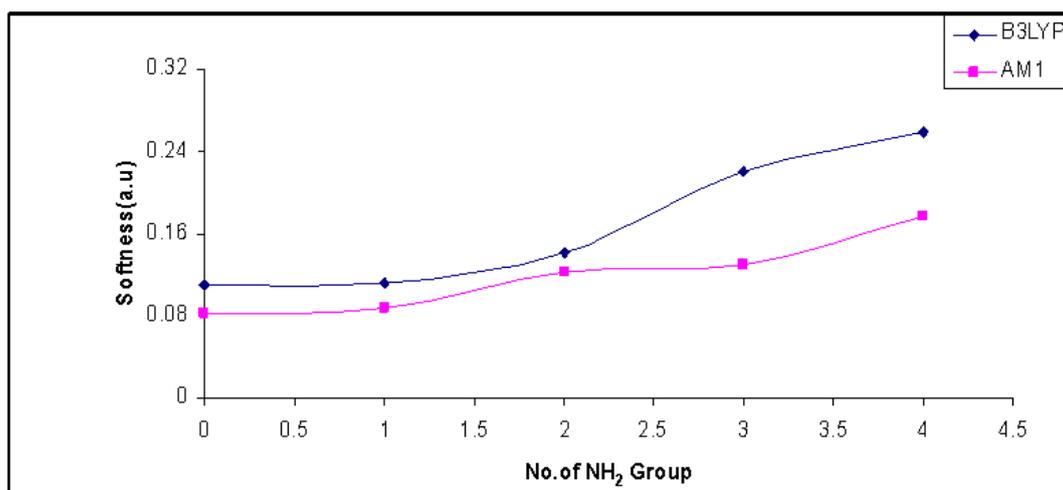


Figure 8. Relation between softness and No. of NH<sub>2</sub> groups

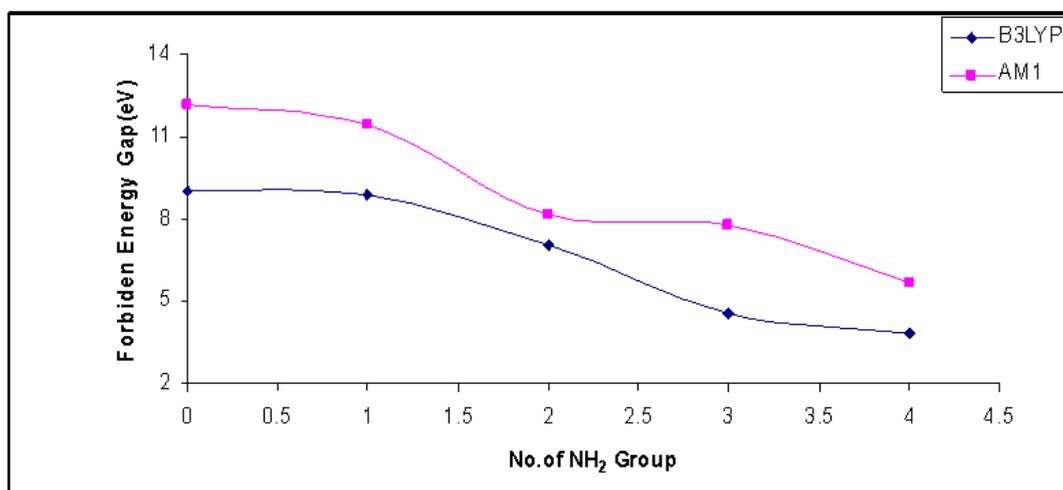


Figure 9. Relation between forbidden energy gap and No. of NH<sub>2</sub> groups

Figure 9 show the relation between forbidden energy gap in (eV) unite and the number of NH<sub>2</sub> groups

calculated by B3LYP/6-31G\*\* and AM1 methods, from this figure can be noted that the energy gap decreases with

the addition of  $\text{NH}_2$  groups. This variation mean that energy gap of tetrahydrofuran molecule will be soft with adding more and more groups.

## 4. Conclusions

1. One of the important results was obtain in this study, is the decreasing of the total energy, bonding energy and forbidden energy gap for all molecules. This declares that these molecules have more stable than organic molecule, also lead to get new semiconductor with more conductivity because the both HOMO and LUMO levels become more adjacent.

2. The total energy, ionization potential, chemical potential, hardness and forbidden energy gap increases with increasing of number of  $\text{NH}_2$ .

3. The electronic affinity and softness decreases with increasing of number of  $\text{NH}_2$ .

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