

## Theoretical Study of Acid Acetylation of Aniline

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The acetylation of amines is one of the most frequently used transformations in organic synthesis as it provides an efficient and inexpensive means for protecting amino groups in a multistep synthetic process.

Acetylation of amine is a nucleophilic substitution reaction. This reaction can be catalyzed by Brønsted acid. In the mechanism, the acetic anhydride first accepts a proton at the carbonyl oxygen and this change enhances the positive charge on the carbonyl carbon. This protonation facilitates the successive addition of amine at the position to form a tetrahedral intermediate, determining step of the rate of the reaction.

Computational method to study the reaction using acid catalysis [1] and an experimental work [2], agreed that this reaction takes place with the formation of a tetrahedral intermediate.

A theoretical study of acid acetylation of aniline from the analysis of intermediate of the reaction was carried out. Geometries of all species involved in the acetylation were made and identified. All of the geometry optimizations were performed by the method at the DFT - Density Functional Theory [3] with B3LYP level of theory and was adopted the 6-31G\* basis set. Energies of all reagents and products and the energy of activation for the reaction were calculated using the MP2- 2<sup>nd</sup> order Mo/ller-Plesset method. Following the same procedure it was identified the geometric parameters and energy of intermediate.

Figure 1 show the optimized structure of the intermediate and the Table 1 lists the geometric parameters, lengths and binding angles values, obtained. The calculations show 18.37 kcal/mol of activation energy.

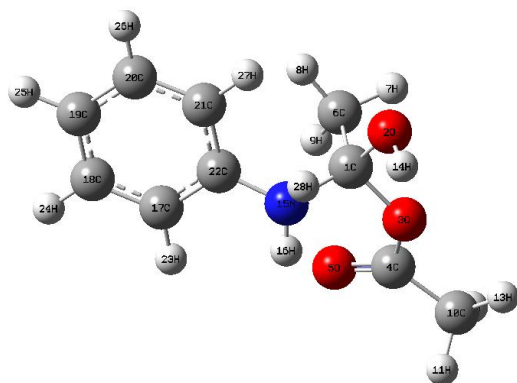


Figure 1. Tetrahedral Intermediate

Table 1. Geometric Parameters Intermediate

Lengths	Å	Angles	°
r (C <sub>1</sub> -O <sub>2</sub> )	1.41	θ (C <sub>1</sub> -O <sub>2</sub> -H <sub>14</sub> )	108.89
r (C <sub>1</sub> -N)	1.47	θ (C <sub>1</sub> -N-H <sub>16</sub> )	106.56
r (O <sub>2</sub> -H <sub>14</sub> )	0.97	θ (N-C <sub>1</sub> -O <sub>3</sub> )	109.60
r (C <sub>1</sub> -C <sub>6</sub> )	1.54	θ (C <sub>6</sub> -C <sub>1</sub> -O <sub>3</sub> )	110.50
r (C <sub>1</sub> -O <sub>3</sub> )	1.46	θ (N-C <sub>1</sub> -O <sub>2</sub> )	112.97
r (N-H <sub>16</sub> )	0.97	θ (C <sub>6</sub> -C <sub>1</sub> -O <sub>2</sub> )	107.05

### References

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2. H.S. Prasad, G.R. Srinivasa and D. Channe Gowda, Synth. Commun., 35, 2005, 1189.
3. C. Lee, W. Yang and R.G. Parr, Phys. Rev. B, 37, 1988, 785.