DFT Study of Acetaldehyde and Isophorondiamine Reaction Mechanism

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Abstract

In this study, it was theoretically investigated which of the two different amine (-NH2) groups in the isophorondiamine (IPDA) molecule would react while forming Schiff base. By optimizing the transition states (TS) and intermediate products (IN) of two different Schiff bases (L1 and L2), their energy and frequency values are calculated using DFT B3LYP method and 6-31+G(d,p) basis set with Gaussian package program. All frequency values obtained in a normal frequency calculation are expected to be positive. If all frequency values are positive, it means that all vibration and rotational movements of the molecule are optimized to the minimum. On the other hand, in transition states, the molecule transitions from one state to another, and the movement showing this transition in frequency values is expected to be negative. The decisive step of this reaction is the TS2 transition, which is the second transition state of the reaction. The energy values calculated for the L1 and L2 ligand using the DFT method are 248.22 kJ/mol and 249.21 kJ/mol, respectively. According to the DFT calculations, which is in good agreement with literature, it was determined that the Schiff base would be formed by the amine (L1) which has less steric hindrance.

Keywords: *DFT, Schiff base, IPDA, Transition state*

1. Introduction

Schiff bases are compounds containing carbon-nitrogen double bonds (-HC=N-), obtained as a result of the nucleophilic addition reaction of aldehydes or ketones with amines. While the bond formed as a result of the reaction with aldehyde is called azomethine or aldimine, the bond formed as a result of the reaction with ketone is called imine or ketimine. Schiff bases (imines) have become among the compounds of interest because they are stable and easy to synthesize [1]. While aromatic aldehydes, which have a particularly effective conjugation system, form stable Schiff bases, these aliphatic aldehydes are unstable and polymerize easily [2]. Schiff bases are some of the commonly used organic compounds. They are used as pigments and dyes, catalysts, intermediates in organic synthesis, and polymer stabilizers. Schiff bases have also been shown to exhibit a wide range of biological activities, including antifungal, antibacterial, antimalarial, antiproliferative, anti-inflammatory, antiviral, and antipyretic properties. Imine or azomethine groups are found in a variety of natural, naturally derived and non-natural compounds. The imine group present in such compounds has been shown to be critical for their biological activity [3].

It is known that Schiff bases, which contain nitrogen attached to the imino group as a donor atom in their structure, easily form complexes with metals through the free electron pairs in the nitrogen atom. The complexes they form with transition and heavy metals have a wide range of uses in environmental chemistry, biochemistry, agricultural purposes, pharmaceutical and dye industries. Schiff bases and their complexes are a subject studied in many important areas such as reversible oxygen binding, catalytic activities in the hydrogenation of olefins, electrochemical electron transfer, photochromic properties and complex formation with some toxic metals. It is also an important class of ligands and has had a very wide field of study in coordination chemistry to date [4]. The synthesis scheme of Schiff bases is shown in Figure 1.

In this study, optimization and frequency calculations of transition states (Transition State (TS)) and intermediate products (IN) in the mechanism of the Schiff base consisting of benzaldehyde and isophorondiamine (IPDA) were made with the DFT/ B3LYP method, 6.31+G(d,p) basis set. The expected vibration movements in the transition states obtained as a result of frequency calculation were observed. By comparing the energies of the transition states and intermediate products in the mechanism from the Gaussian outputs obtained, it was determined

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theoretically which amine group would be more ideal to bind to for the formation of a Schiff base.
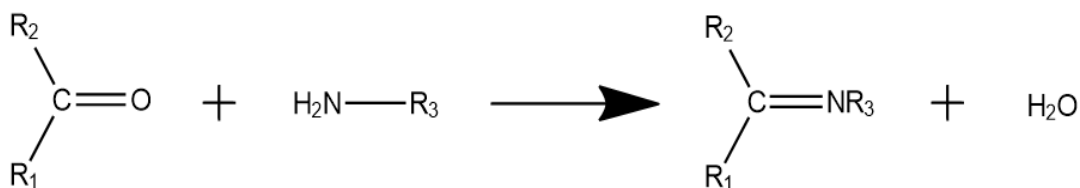

Figure 1. Synthesis scheme of Schiff bases

2. Material and Method

Within the scope of this study, the formation mechanism of benzaldehyde-IPDA Schiff base from both amine ends was drawn with the Chemdraw program. All modelled molecules, reactants, intermediates (IN), transition states (TS) and products were calculated using density functional theory (DFT/B3LYP) [5] and the 6,31+G(d,p) basis set. Frequency calculations of all molecules were also made and it was proven that they were calculated in the correct geometry. Gaussian 09 program [6] was used in all calculations. The formation mechanism of the Schiff base from the first (L1) and second pathway (L2) is given in Figures 2 and 3.
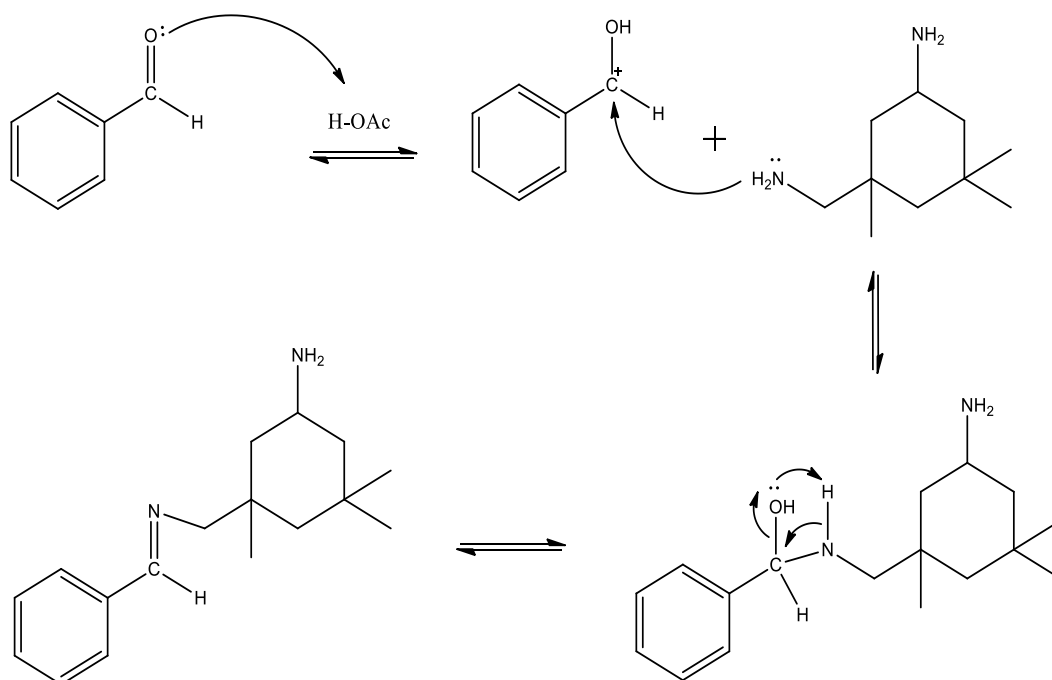

Figure 2. Schiff base mechanism: 1st path (L1)

3. Result and Discussion

Schiff base formation reactions generally begin with the nucleophilic approach of the amine group to the carbonyl carbon in the presence of catalysis. For this approach, the first transition state (TS1 and TS1a) was modeled and calculated using the DFT/B3LYP method and 6-31+(d,p) basis set. Frequency calculations were also made using the same method and basis set. Calculating the single negative frequency in the molecules indicates that the correct TS molecule has been captured. Optimized geometries for TS for both paths are given in Figure 4.

As a result of the unpaired electron pair in the amine (-NH$_2$) group approaching the carbonyl carbon, a single bond is formed on carbon and nitrogen through the TS transition state, forming carbinolamine intermediates. The intermediates formed for both mechanism proposals, IN1 and IN1a, are depicted in Figure 5.
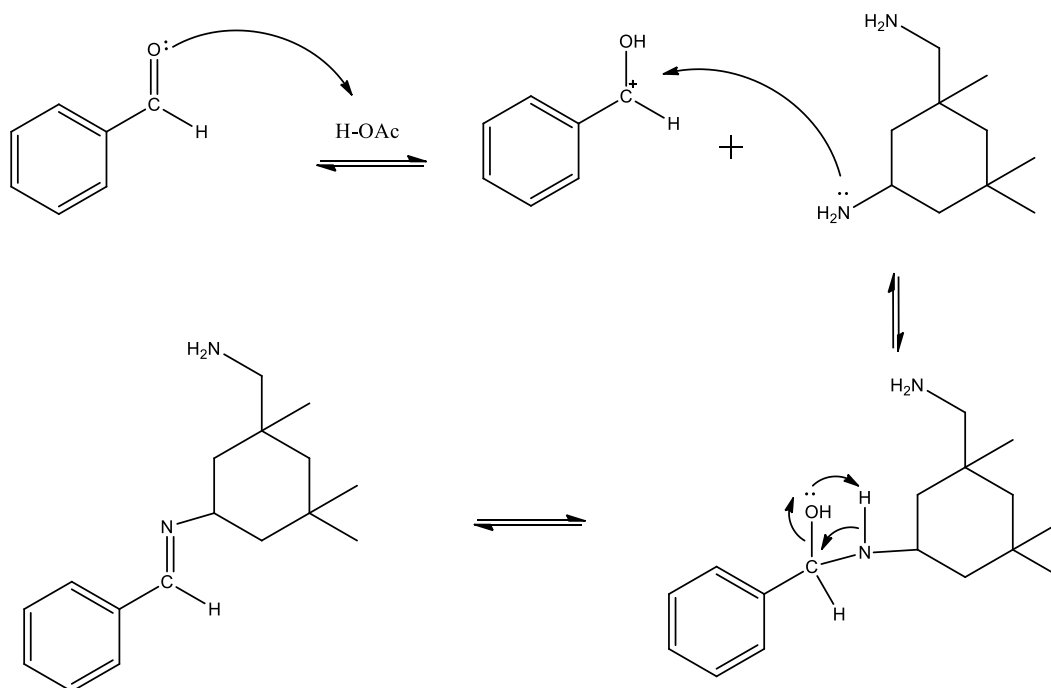
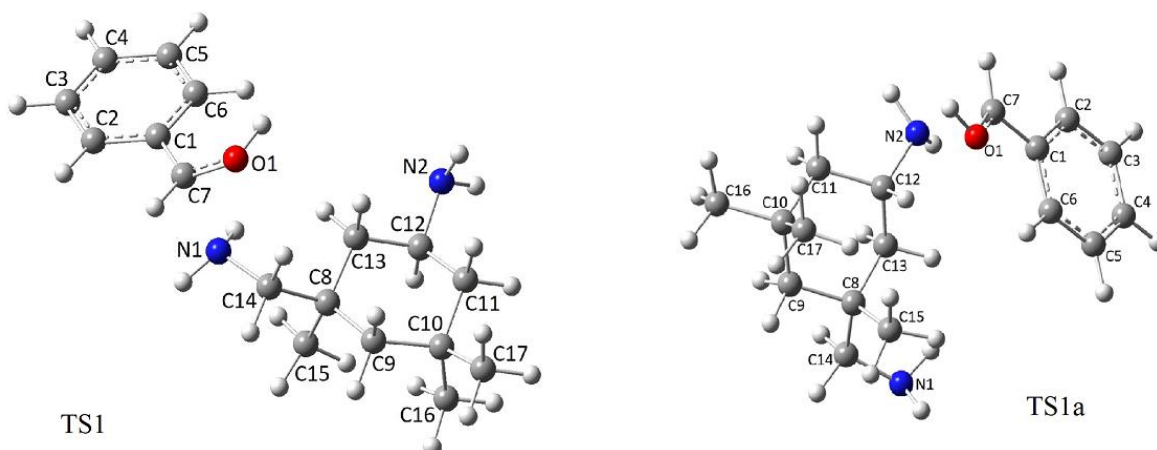Figure 3. Schiff base mechanism: 2st path (L2)

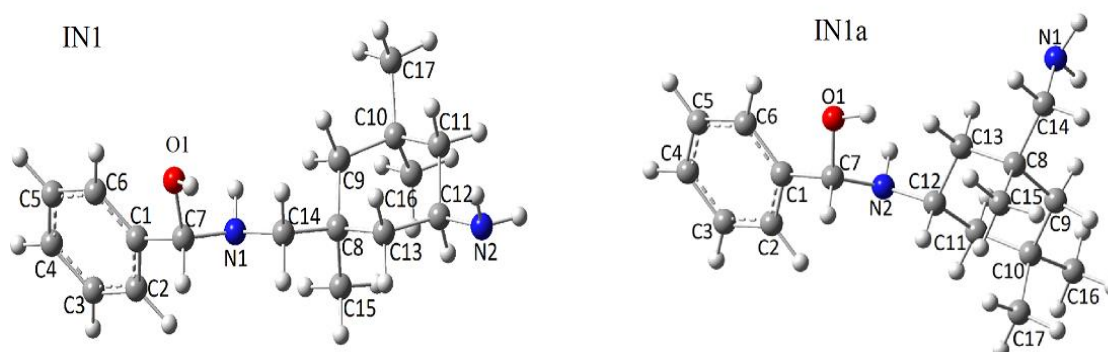Figure 4. Optimized structures of TS1 and TS1a

Figure 5. Optimized structures of IN1 and IN1a

In the last step of the reaction, Schiff base molecules are formed by separating -OH2 from the product through the TS2 transition state, where the -NH proton in the resulting carbinol amine approaches

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oxygen. The optimized structures of the intermediate products (TS2 and TS2a) in this step are given in

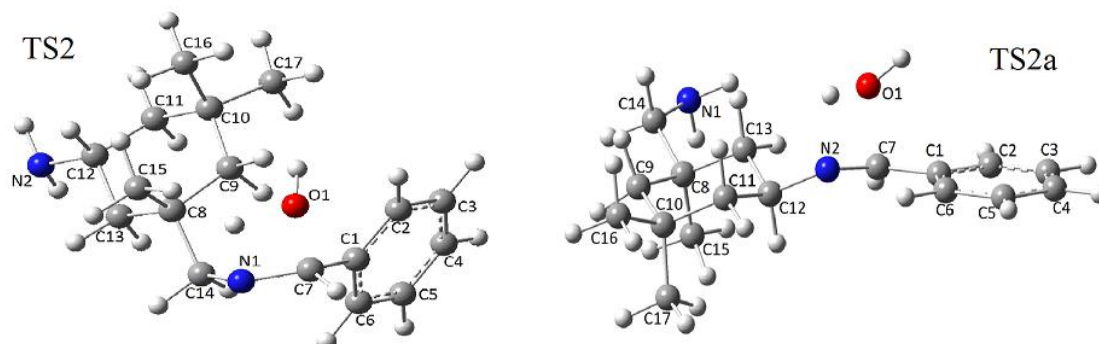Figure 6, and the optimized structures of the final products are given in Figure 7.

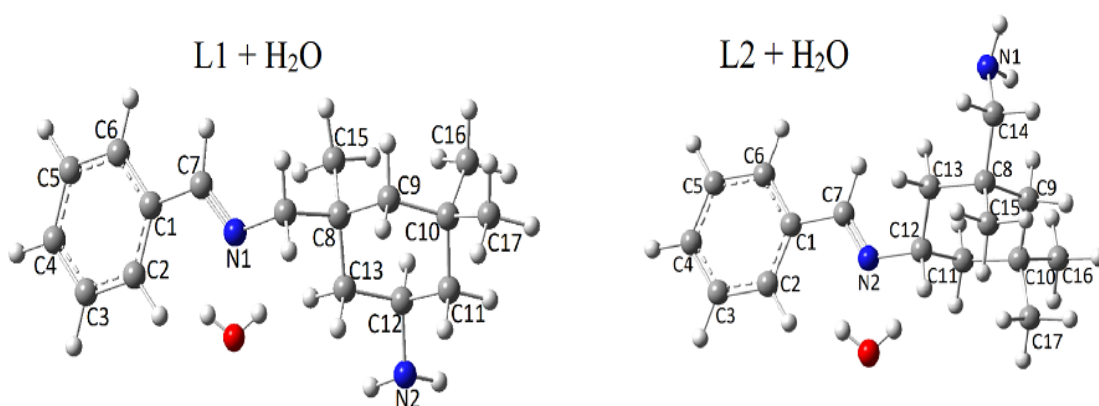Figure 6. Optimized structures of TS2 and TS2a

Figure 7. Optimized structures of products (L1 and L2)

The free energy values and frequency calculations of the molecules given in Figure 4-7 were calculated using the DFT/B3LYP method and the 6-31+G(d,p) basis set and are listed in Table 1. When Table 1 is examined, it is seen that the step that determines the rate of the reaction is the second step, the transition step of the proton on nitrogen to oxygen in carbinol amine.

Table 1. Free energy and negative frequency of reactants, intermediates, transition states and product molecules

Molecules	Free energy (kJ/mol)	Negative frequency
Benzaldehit + IPDA	0	-
TS1	121.43	-148.35
IN1	-10.52	-
TS2	248.22	-1466.87
$L_1 + H_2O$	-20.46	-
Benzaldehit + IPDA	0	-
TS1a	125.18	-145.46
IN1a	3.28	-
TS2a	249.22	-1532.49
$L_2 + H_2O$	-29.64	-

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The energy values of the transition states of this step, TS2 and TS2a, were calculated as 248.22 and 249.21 kJ/mol, respectively. These results support that the first route is preferred and show that it reacts with NH2 in the -CH_2NH_2 group. These results also support the experimental results in the literature [7,8].

4. Conclusions

There are two different amine (-NH2) groups in the isophorondiamine (IPDA) molecule. There are very few experimental studies on which amine end this molecule will join when it reacts with carbonyl-containing aldehydes or ketones. It is important that these experimental studies are supported theoretically. Within the scope of this study, it was modelled considering that it could participate in the reaction from both amine ends, and the reaction mechanisms were calculated for both pathways. According to the calculation results, it was determined that the step that determines the rate of the reaction for both mechanisms is the second step and that the transition state in the first proposed mechanism has lower energy (TS2<TS2a). These results show that it will participate in the reaction from the end where the steric effect is low, as in experimental studies.

References

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