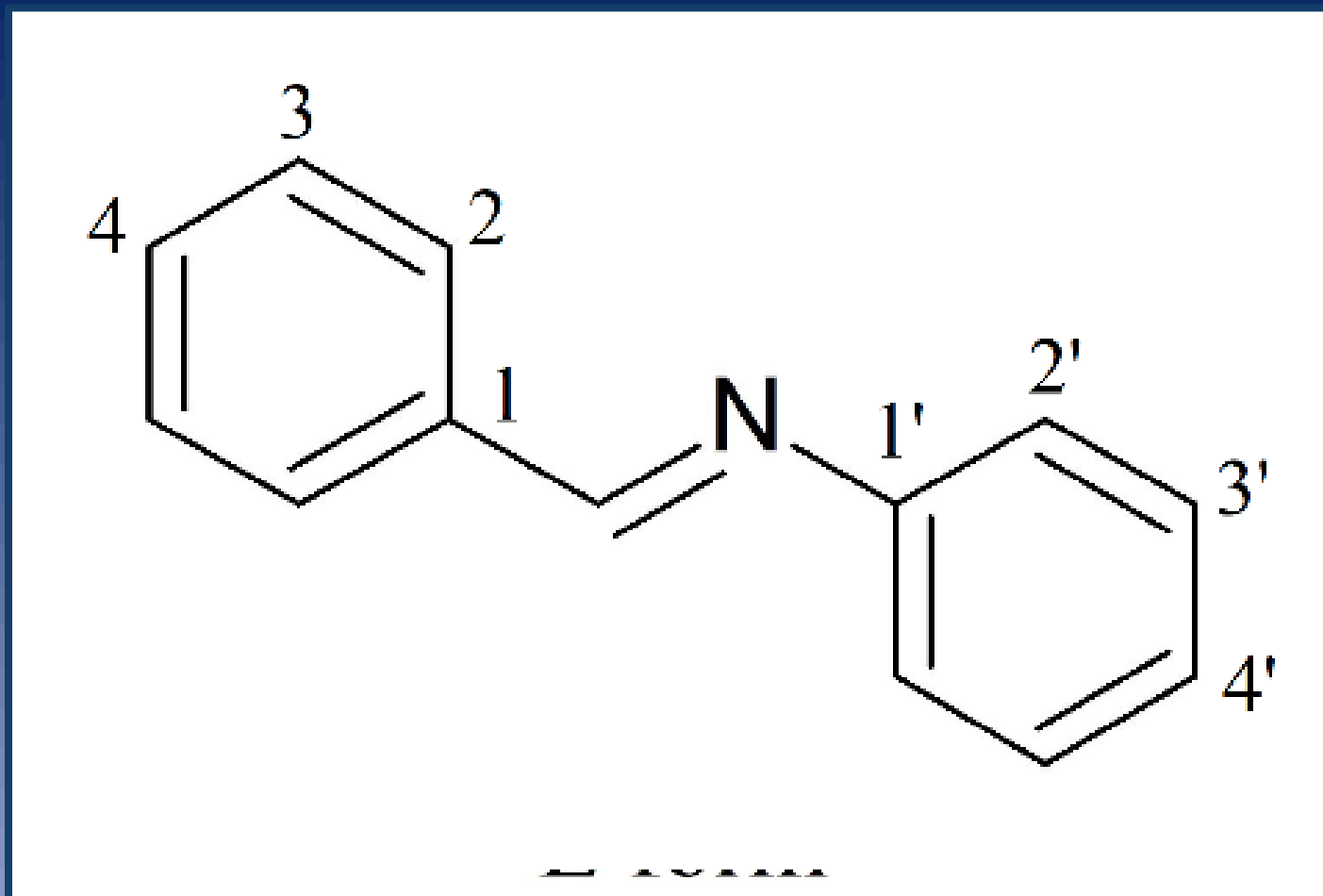




A DFT AND EXPERIMENTAL STUDY OF THE HYDROLYTIC DEGRADATION BEHAVIOUR OF SOME BENZYLIDENEANILINES: TOWARDS THE DEVELOPMENT OF OPTICAL METAL SENSORS

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Abstract

A thorough experimental and Density Functional Theoretical (DFT) investigation of the spectroscopic and hydrolytic degradation pathways of some simple benzylideneaniline derivatives is conducted, revealing that the 2-aminophenol derivatives undergo significantly faster hydrolysis than other derivatives due to the involvement of the 2'-OH group in their hydrolysis mechanism. Whereas for the 2-hydroxyaniline derivatives the second step is rate-limiting, for compounds without this structural feature, the first step is slowest. The absence of this 2'-OH group leads to increased hydrolytic stability of benzylideneanilines and thus better candidates for optical sensors for the detection and quantification of a toxic heavy metal, copper, in water.

Introduction

Benzylideneanilines, are commonly applied as optical sensors for the determination of various analytes, heavy metals being chief among them. These compounds are known to act as both colorimetric and fluorimetric sensors for various metal ions. However, the susceptibility of the C=N moiety to hydrolytic cleavage is limiting, therefore, it is crucial that the hydrolytic stability of potential sensors be considered, particularly those being considered for application in aqueous environments. Susceptibility to hydrolysis is greatly a function of structural and electronic factors. Preliminary studies have revealed 2'-hydroxybenzylideneanilines to be especially reactive in this regard; however, no in-depth study of the kinetics and thermodynamics of this reactivity has been reported. Hence, in this study, the hydrolytic degradation behaviour of these compounds is probed from a fundamental perspective using both experimental and molecular modelling techniques with the aim of understanding the factors driving this process such that sensors offering greater hydrolytic stability can be designed. Indeed, such systems will allow easy analysis of water samples for heavy metals by novice analysts in the field.

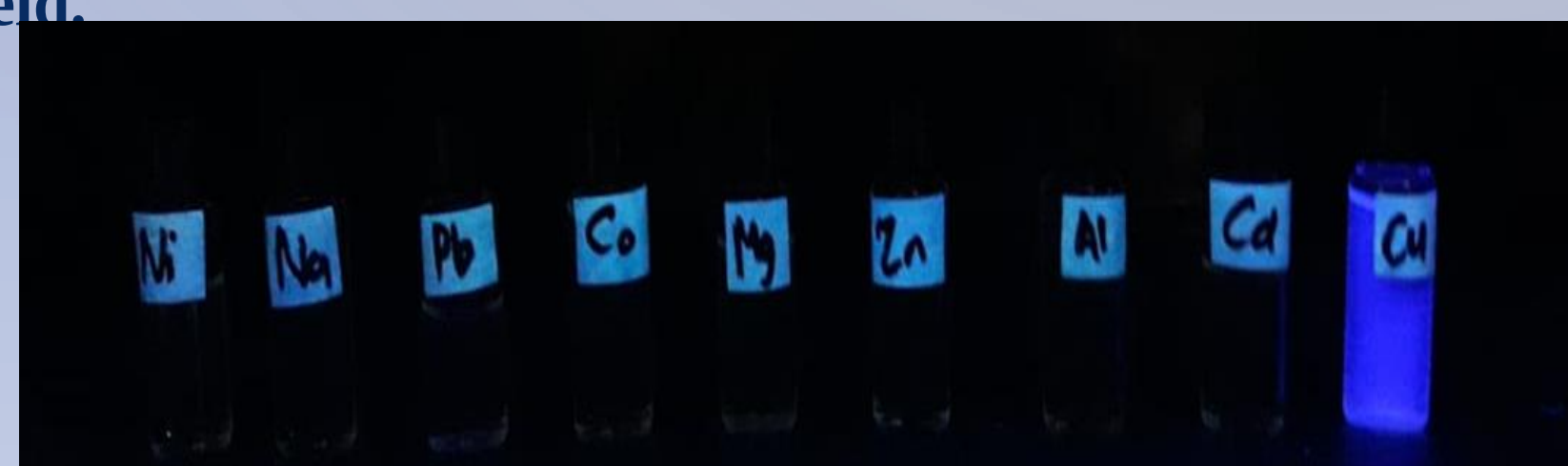
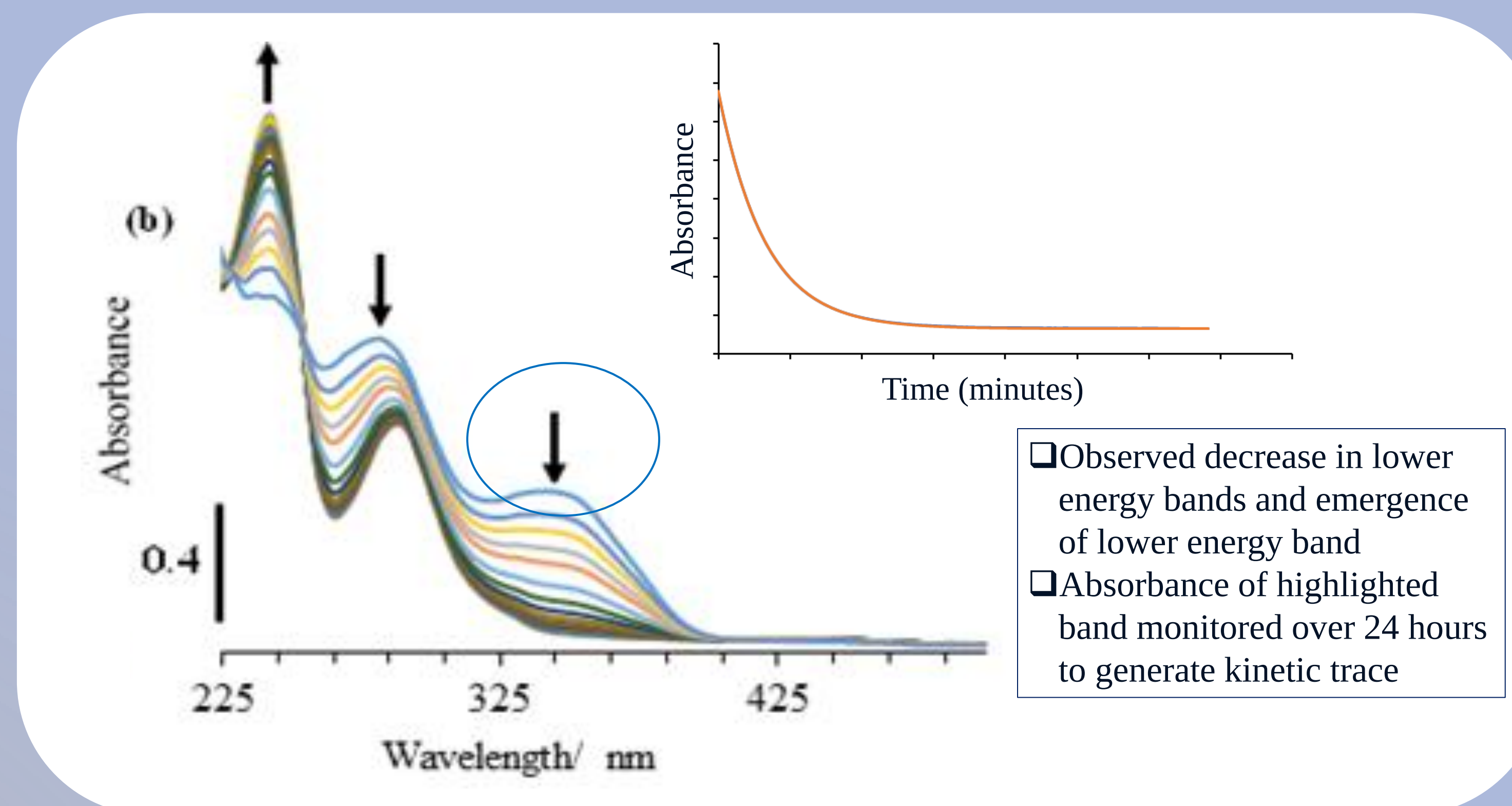


Figure 1. Changes in the spectrum of 2'-hydroxybenzylideneaniline during hydrolysis, observed over 24 hours

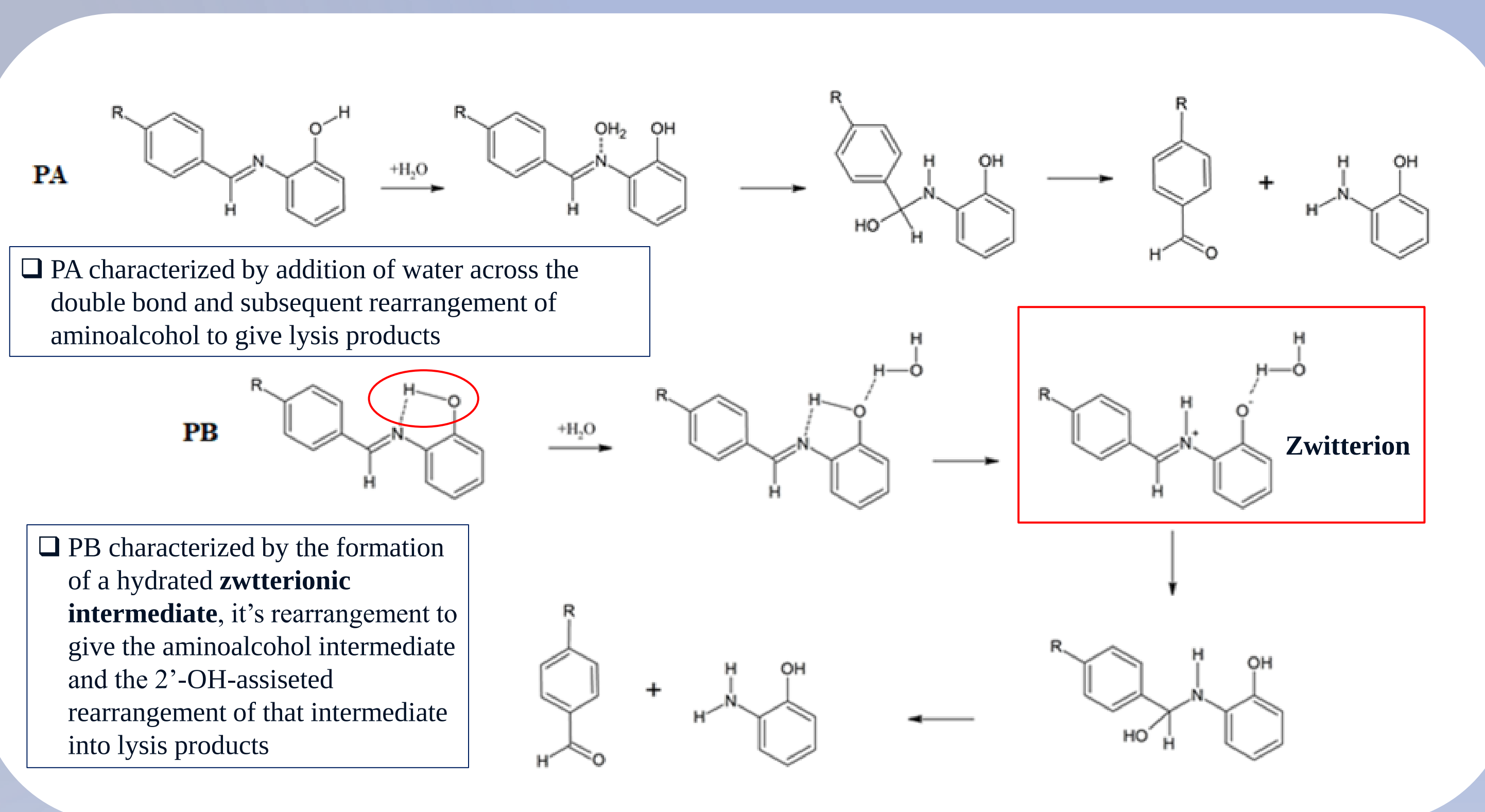


Figure 2. General mechanism for hydrolysis of benzylideneanilines (PA) and proposed mechanism for hydrolysis of 2'-hydroxybenzylideneanilines (PB)

Results and Discussion

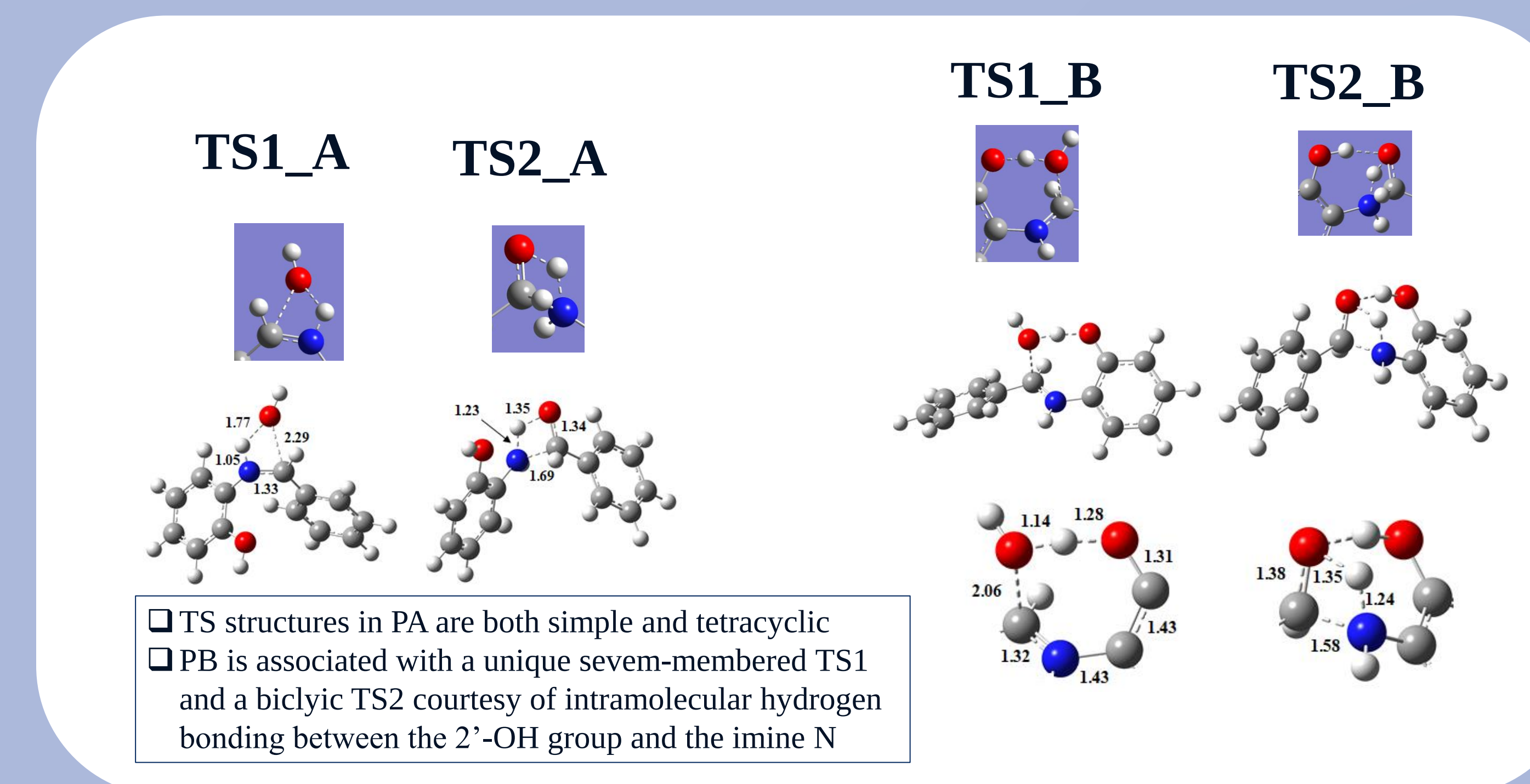
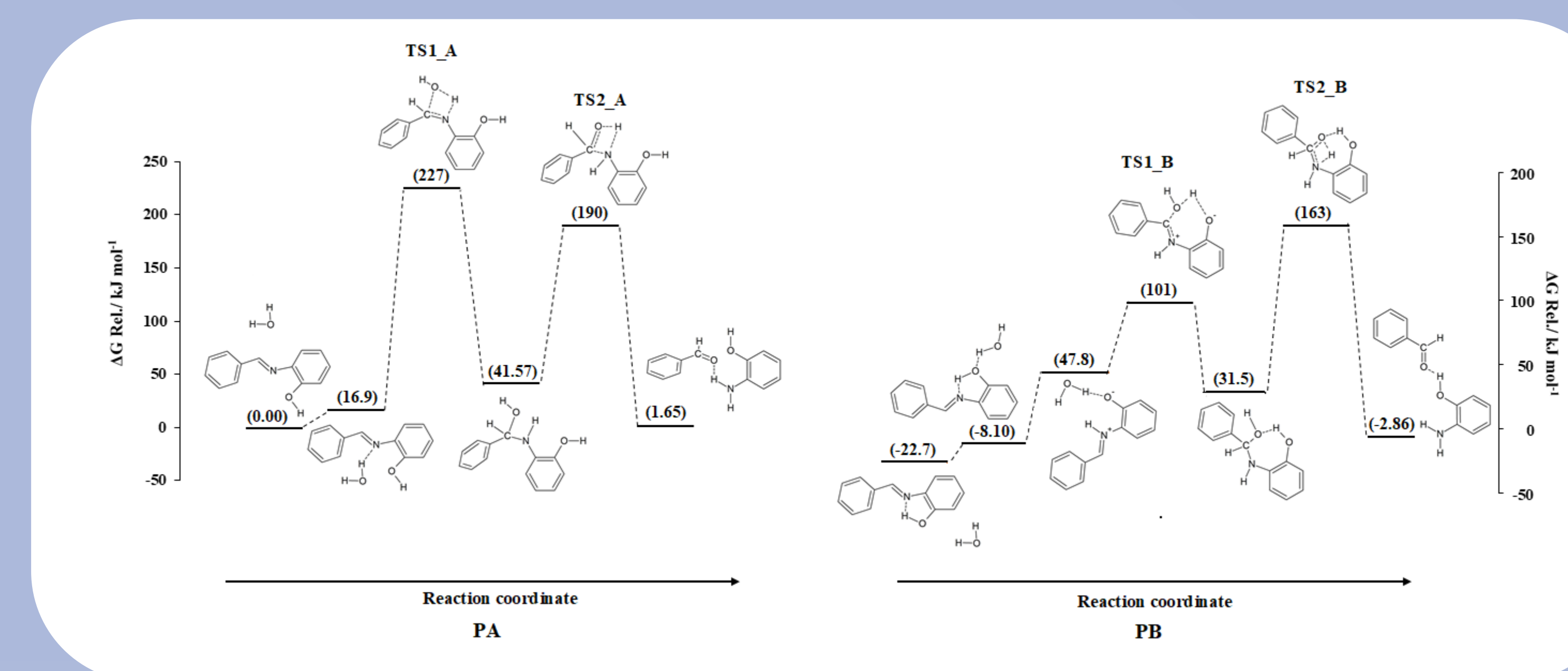


Figure 3. Optimized transition state structures for 2'-hydroxybenzylideneaniline for PA (left) and PB (right), respectively



The 2'-OH group plays an important role in the mechanism given by PB:

- It leads to the formation of a zwitterionic species that transforms into a seven-membered transition state
- It anchors adjacent reaction sites to facilitate the degradation of the intermediate in the 2nd step

Conclusion

Benzylideneanilines with a 2'-OH likely undergo hydrolysis via a mechanism where this group plays a critical role in both major steps- in the first, providing for the formation of a zwitterionic intermediate which leads to an exceptionally stable seven-membered transition state; in the second, it acts as an anchoring group to facilitate the degradation of the second transition which is the rate-limiting step.

Compounds without this structural feature will hydrolyse via the more well-known less energetically-conservative pathway. Ultimately the results obtained via molecular modelling studies help to rationalize the spectroscopic features and the hydrolysis kinetics and thermodynamics of the titled compounds