ABSTRACT: In the early seventies received wide attention when Patai [1] published his book tagged the chemistry of the azomethane group and the aforementioned group is very important in the fields of chemistry, life sciences, chemical and pharmaceutical industries and medicine. The chemistry of imines includes two main groups is Schiff bases and oximes. as well as presence of double bonds in the imines facilitated the possibility of their presence in the form of two Geometrical Isomers. Curtin and Husser [2] are among the first to discover the presence of imines in two forms, syn and anti, and the inability to separate these two forms in the imines is attributed to the freedom to rotate around the double bonds between The carbon and nitrogen atoms, which reduce the occurrence of the polarization process in C=N and facilitate the rotation process [3].

Keywords: tautomerism, organic chemistry, azomethane group

INTRODUCTION

The oximes are another class of the imines compounds, and these compounds are present in two [4] space forms, which are anti, syn, since these forms [3,4] are determined according to the location of the hydroxyl group associated with the active group C=N, since the spatial shape of the syn isomer is the one that In it the hydroxyl group is close to or on one side of the hydrogen atom or the alkyl groups associated with the carbon atom present in the active group and towards it. As for the stereo type of the anti-isomer, the hydroxyl group is opposite to the direction of the hydrogen atom associated with the carbon atom in the active group. Replacing the hydrogen aldehyde with the R-group leads to obtaining keto oxime. The reason for the presence of the oximes on two isomers due to the presence of double bonds between the carbon and nitrogen atoms connected to the other end of the hydroxyl group.

Study [1] confirmed that there are major differences in the physical properties, including the natural properties of the isomers, which confirms the development of the word anti, syn when it is called. The terms (syn) and (anti) in the oximes are found similar to that in the engineering isomers, which are (cis) and (trans), respectively, in addition to the presence of two other terms for the oximes, symbolized for them. (Alpha) for the isomer (Syn) stands for (Beta) for the isomer anti. The researchers used [1] the symbols (Z) and (E) to denote the isomer, anti, syn, respectively. The last two symbols have been used mostly in the chemical software of the oximes and Schiff bases mentioned above.

The researchers used [1] several physical and chemical methods to diagnose the isomerism in oximes such as dipole moment and dielectric constant and chemical reactions such as esterification of oxime, but all these mentioned technologies or interactions were subject to doubt, inaccuracy and harmony when applied to Various and different oximes. That is, it gives mixed results as for the study [5] conducted by Azzouz, it removed the recent complications and doubts about the stereochemistry of oximes, as it used the integrated ion current curve technology to diagnose the engineering isomers in the oximes. The last method is a spectral technology used in mass spectrometry. It is a fast, economical and accurate method that can be applied to schiff bases and other organic isomers.
**RESULTS AND DISCUSSION**

**Tautomerism of para-Aminobenzylidene-para-methoxyaniline**

The UV spectrum was studied for the Schiff base of the p-AB-p-MA at a concentration of $0.25 \times 10^{-4}$ M in ethanol. The study reached two peaks with wavelengths of 324.8 nm, 235.6 nm and molar absorption coefficient of 6.26 $\times 10^{-4}$ and 4.34 $\times 10^{-4}$ in units (liter.Mole$^{-1}$.cm$^{-1}$) respectively. These two peaks are due to the presence of two chromophore groups in the compound, one of which is the aldehyde ring with the azomethine group at one level and the other the first amine ring. This statement is consistent with the findings of AlBayoumi [6] when studying the UV spectrum of the Schiff base of the benzylideneaniline. The spectroscopy of the U.V spectra was repeated for the same compound but after adding concentrations of Na$_2$CO$_3$ with a range between $(5.0 \times 10^{-3} - 0.5 \times 10^{-3})$ M. The obtained results, which show the appearance of three different peaks of intensity, recorded the first and second peaks, their locations differing from the peaks of the original spectrum. Therefore, they can be traced back to the interaction of the tautomerism that occurs in the compound shown in the following diagram

![Diagram showing amine and imine forms](image)

This kind of tautomerism can happen in the compound under study, which is the transfer of a proton from atom (1) to atom (3) 1,3-proton Shift, and this is consistent with the literature [7-9]. The optimum conditions were studied for the reaction of tautomerism Schiff base (p-AB-p-MA) where the concentration of Schiff base $(0.25 \times 10^{-4})$ M was constant but different concentrations of sodium carbonate and it was found that the best carbonate concentration was $2.5 \times 10^{-4}$ M which gives the best absorption of the first and second peaks when compared to the rest of the values.

The researcher suggested that the first peak with a wavelength of 321.2 nm with absorbance value of 0.989 is attributed to the amine tautomer and the second peak with absorbance wavelength of 232.2 nm with a value of 0.875 due to the imine tautomer. This was accepted and agreed in literature with tautomerism [10] of imines, which showed an absorbance peak of the imine tautomer at the shortest wavelength.

This latter confirmed in this study that the reaction of tautomerism leads to a break in the aromatic ring of the aldehyde molecule in the Schiff base and to support this last when comparing the molar absorption coefficient values of the peaks of the amine form and the imine form, which showed molar absorption coefficients of 3.95 $\times 10^4$ and 3.5 $\times 10^4$ in units (liters . Mole$^{-1}$.cm$^{-1}$), which is lower than the original peak values of the compound before adding the base value of $6.26 \times 10^4$ and $4.34 \times 10^4$ in the same previous units.

**Effect temperatures on tautomerism (p-AB-p-MA)**

The study included measuring the U.V spectra at limited temperatures between (10-50) °C with Na$_2$CO$_3$ and at the optimum conditions indicated where at 10 °C absorbance values of $(A_1)$ were equal to 0.93, absorbance values of $(A_2)$ were equal to 0.779 at 20 °C absorbance values of $(A_1)$ were equal to 0.92, absorbance values of $(A_2)$ were equal to 0.85 at 30 °C absorbance values of $(A_1)$ were equal to 0.905, absorbance values of $(A_2)$ were equal to 0.89 at 40 °C absorbance values of $(A_1)$ were equal to 0.89, absorbance values of $(A_2)$ were equal to 0.94 and at 50 °C absorbance values of $(A_1)$ were equal to 0.88. Absorbance values of $(A_2)$ were equal to 1.00, $(A_1)$ equals the absorbance in wavelength $s\lambda_1$ nm is equal 321.4 nm, $(A_2)$ equals the absorbance values in the wavelengths $\lambda_2$ nm is equal 233.6. A graphic relationship between the $(A_1)$ and $(A_2)$ absorptions against the T °C we obtained linear relationship between $A_1$ and T °C and its inverse linear relationship between $A_2$ and T °C and the values of the
correlation coefficients $R^2$ are equal to 0.9941, 0.9929, respectively. When plotting a linear relationship between $A_1$ and $A_2$, the result was to get a linear inverse relationship with a value of $\alpha_{1a2}$ equal to 0.2421.

The value of $R^2$ is 0.9754 and gave a graph of a relationship between lnK against $T^{-1}$, and the value of $R^2$ is 0.9682. The standard thermodynamic variables, $\Delta G^0$, $\Delta H^0$, and $\Delta S^0$, were calculated for Schiff base-tautomerism reactions (p-AB-p-MA) based on the standard equations and equaled $3.61610.0 J.mol^{-1}$, 4.58043 KJ.mol$^{-1}$, 3.18 J.mol$^{-1}$K$^{-1}$, respectively. $\Delta H^0$ was calculated using the Van't Hoff equation and lnK diagram against $T^{-1}$ gave a straight line with an inverse relationship and $R^2$ value is 0.9682. $\Delta G^0$, $\Delta H^0$, $\Delta S^0$ values is a positive sign, these mean that the front tautomerism reaction with the Schiff base under study occurred in non-spontaneous process, endothermic, is accompanied by an increase in random of system. Finally, this study was identical to previous studies [10,11] and after adding the base Na$_2$CO$_3$.

**Effect of buffer solution on tautomerism (p-AB-p-MA)**

This clause included a study of the effect of different buffer solutions peaks with pH values [4,6,7,8,9,10] on the spectra of the Schiff base with a concentration (0.25x10$^{-4}$M). And obtained a spectrum similar to the original spectrum mentioned previously and after adding the base with a slight difference in their wavelengths, and this is expected due to the difference in the acidic and basic media used in this study.

The shape of the seven U.V spectra of the Schiff base of under the study obtained by the mentioned above acidic functions, in which all the spectra are similar, which indicates that they are not affected by the different acidic functions. The two peaks were attributed by high and low wavelengths to the amine and imine tautomer, respectively. This is because of the increase in the absorption of the amine tautomer with an aromatic characteristic compared to the amine tautomer with a partial aromatic character of the original aldehyde molecule. This last talk is expected from the theoretical point of view, meaning that any breakdown of the aromatic system is accompanied by a decrease in absorption or the availability of the compound or tautomer.

$A_1$, $A_2$ equals absorbance value at the wavelength 321.2nm, 233.2 (nm) respectively, at pH4 $A_1$, $A_2$ equals 1.309, 1.109, at pH6 $A_1$, $A_2$ equals 1.115, 0.922, At pH7 $A_1$, $A_2$ equals 1.481,1.256, at pH8 $A_1$, $A_2$ equals 1.423,1.208, at pH 9 $A_1$, $A_2$ equals 1.354,1.149, at pH10 $A_1$, $A_2$ equals 1.415,1.208 noting.

(p-AB-p-MA) is not affected by the different buffers. The latter means the difficulty of tautomerism form of the stable amine compound to the less stable imine form. The nitrile or oxonium ions do not appear in the acidic functions and in the high wavelengths as we have observed with a study day (p-AB-p-MA), which means that it does not stabilize and does not form with the mentioned functions.

**REFERENCES**
