



## Thermodynamic study for the stability of aromatic complexes formation derived from the reaction of 4-dimethyl amino benzaldehyde with diazotized dinitro aniline reagents



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### Abstract

This research includes the preparation of aromatic azoimine complexes resulting from the coupling reaction (4) of Schiff bases with diazotized dinitroaniline reagent. Ultraviolet spectra, infrared spectra, and melting points are among the most important physical methods used to identification the right compounds prepared in this study. After that, the stoichiometric ratios of the components of the complex were determined using the molar ratio method, and we got a ratio of (1:1) for all the studied complexes. Finally, the factors that affect the stability constant values were studied, namely:

- A-Effect of acidity function: These stability constants were studied for each of the prepared complexes at each acidic function (pH) and different temperatures, and we obtained values for the stability constants, which are evidence of the preparation of stable azo complexes.
- B-The effect of temperature: These stability constants were calculated at a range of temperature (313–273°K) which allowed us to know that the reactions of formation of azo dyes are spontaneous and exothermic from the negative values of ( $\Delta G^\circ$  and  $\Delta H$ ) respectively, as well as the negative ( $\Delta S^\circ$ ) value that supports what was mentioned previously.
- C-Effect of Structure: The type of functional group and its location also has an effect on the values of the stability constants of the prepared complexes, and this was proved by the variation in the values of the stability constants.

**Keywords:** aromatic imine complexes, thermodynamic parameters, diazotized reagent, Schiff base, stoichiometric ratio , stability .

### 1. Introduction

The imine is known as an organic chemical compound that includes a double bond linking carbon with nitrogen ( $-C=N-$ ), and it replaces an oxygen atom with a nitrogen atom to turn ketones and aldehydes into organic compounds, which are imines (Serban C. Moldoveanu. , 2019). Schiff bases are condensation products of aliphatic or aromatic primary amines with carbonyl compounds such as aldehydes or ketones. Schiff bases contain a common structural functional group for these compounds, the azomethine group, whose general formula is  $RHC=N-R_1$ , where R and  $R_1$  are alkyl, aryl, cycloalkyl groups or heterocyclic groups which can be substituting by differently substituents. There is competition between azomethane functional groups  $C=N$  and carbonyl group  $C=O$ , where carbonyl excels in the ability to

form complexes with positive ions (Cimerman , Z. & Galic , N. , 2000). These compounds are also known as azomethines. The presence of the lone pair of electrons in the  $sp^2$  hybrid orbital of the nitrogen atom of the azomethine group is important in terms of its effect on the basic properties of the compounds containing a group of azomethane (Patel P. & Zele S. , 1999) (Elmali A. & Elerman Y. , 2000). The stability and properties of Schiff bases are greatly influenced by the carbonyl compounds and the type of amine derived from them, whether aromatic or aliphatic. The presence of functional groups that have a large electrical negativity related to the imine nitrogen reduces the polarization formed by electrostatic repulsion and the reason is due to the juxtaposition of negative similar charges (Al-Niemi , Mohammad Mahmoud, 2005). In a recent study, stable complexes

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were prepared from coupling Schiff bases with transition metal ions such as  $\text{Cu}^{2+}$ ,  $\text{Pd}^{2+}$ ,  $\text{U}(\text{VI})$ , etc... It was concluded that these complexes are usually stable at heating and many researchs were able to describe their thermal decomposition (Serban C. Moldoveanu, 2019). There are several modern methods for producing Schiff bases, including environmentally friendly ones, as in the green production method. It is economically feasible, without pollutants, easy, and its yield in terms of production is high. The reaction medium is water. The preparation is done from the reaction of 1,2-diamino benzene with aromatic dehydrate, and we get the product by filtering and then washing and drying (Rao. et.al., 2005). Choosing the appropriate solvent and the optimum reaction conditions obtained have the great effect of producing Schiff bases in this way with excellent yields and in one step. Also, one of the advantages of this method is to reduce the reaction time, which means saving the energy needed for production, as well as increasing the conversion rate and reducing waste. The output was confirmed by IR, Mass spectra and  $^1\text{H}$ NMR data. (SAROJ K. SHARMA et al., 2012). In recent years, interest in imines has focused in the health field, as the number of people suffering from cancer and multidrug-resistant infections has increased sharply, leaving humanity with no choice but to search for new treatment options and strategies. Although cancer is considered the leading cause of death worldwide, Schiff bases have been a topic of great interest, due to their versatile chelating properties, inherent biological activities and flexibility in modifying the structure to tune it for a particular biological application. Research in Schiff base based metal complexes is underway to develop new anticancer and antimicrobial chemotherapies and because the anticancer and antimicrobial targets are different, structurally heterogeneous Schiff bases can be modified to achieve the wanted molecule, which targets a specific disease. (Manzoor Ahmad Malik., 2018). The diazotization reaction is taking place to form azo complexes in optimal conditions, the most important of which is the temperature, which should be close to (zero Celsius), and this degree give stability to the resulting salts also increases the solubility of nitrous acid and releases it as a gas (Jonathan Clayden et al., 2012). The electron-pushing groups in the amine increase the stability of the diazonium salt, and on the contrary, the electron-

withdrawing groups reduce its stability. The relative stability of the aromatic diazonium cation can also be attributed to the non-localization of the positive charge on nitrogen in the pi ( $\pi$ ) system of the ring (Arun sethi, 2006). Diazonium salts have many important applications, the most important of which is that they are intermediate compounds of organic synthesis because they have the electrophilic property. This is why they are combined with many compounds of large electronic density. Here we address the most common and important applications of these salts, which are azo dyes. (Mohamed Mehdi Chehim, 2012). Our research focused on calculating the stability constants values of the resulting complexes, through which it is possible to know information related to the quantity or concentration of complexes in the solution. These calculations are very important in many fields of science such as chemistry, biology, and medicine. It was found through a very recent study (Jagvir Singh, et al., 2020) that the stability of complexes is affected by various factors such as the nature of the electron-donating molecule, the bond and the chelating effect, and some parameters such as distribution coefficients, conduction, and refractive coefficients. As for calculating the ratios of the components for the complex, it is intended to determine the quantity of each of the reactants present at the beginning of any chemical reaction and how the products can be formed. The stoichiometric ratio of the complex can be calculated on the basis of the law of conservation of mass, where the total mass of the reactants is equal to the total mass of the resulting complexes, which leads to the realization that the relationship between the amounts of reactants and products is usually a ratio of positive integers. This means that if the amounts of the separate reactants are known, then the product can be computed. Conversely, if one of the reactants has a known quantity and the quantity of the products can be determined empirically, then the quantity of the other reactants can also be calculated. (Carmen J. Giunta, 2016). Estimating the ratios of the components or (stoichiometric ratios) for the complex, i.e. the ratio of the donor to the acceptor, is very necessary to determine the stability constants of the complexes formed. There are a number of methods for calculating the ratios of the components for complexes, including: the gradient ratio method, the oxidative potential method, the solubility method, the molar ratio method (used in our current study). In the molar ratio method,

a group of solutions is prepared in which the molar concentration of the donor (imine) is fixed with an increasing molar concentration of the acceptor (reagent). Then the absorption is plotted against the volume after taking the absorbance of the prepared solutions at the wavelength that gives the highest absorption of the complexes ( $\lambda_{max}$ ), or the ratio of the increased volume of the substance / volume of the fixed substance is plotted and we get two lines in which the point of intersection here represents the molar ratio of the complex formed. (Mansoor Niaz1 and Luis A. Montes2, 2012).

## 2. Experimental part

### 1-Chemicals:

The chemicals used during the research were supplied by Switzerland Fluka, British BDH and Spanish PRS companies: sodium hydroxide, hydroxylamine hydrochloride, ethanol, sodium carbonate, sodium nitrite, hydrochloric acid, 4-(dimethylamino) benzaldehyde, Aniline, o,m and p-Toluden and dinitro-aniline.

All compounds were prepared in a standard manner similar to a previous study (Al-Niemi, Mohammad Mahmoud, 2005). Except for aniline only, which was purified by ordinary distillation, we obtained distilled aniline with a pale yellow color, which boils at a temperature range (178-184°C).

### 2-Instruments:

#### a-UV-Visible Spectrophotometers:

A single beam Spectrophotometer instrument manufactured by the British company (Cecil) (Cambridge England) model (CE 1011/1000) in the range of wavelengths (325-1000nm.).

A double beam Spectrophotometer instrument containing a computer made by the Japanese company (Shimadzu), model (UV-1800) produced in 2004 to check the value of ( $\lambda_{max}$ ) for the complexes under study and draw the different electronic spectra in the water solvent in the range between (190-1100nm.).

The cells used above were: glass in the visible region and quartz in the invisible region.

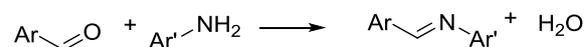
b-pH-meter : Made by (JENWAY) Company, Model (3510).

c-Water bath : Model (D3165) type (Hanigsen) manufactured by (KOTTERMANN) company.

### 3-Preparation of Schiff bases:

Schiff bases were prepared by mixing equal molar amounts of (0.01mole) aldehyde with (0.01mole) of the aromatic primary amine that was dissolved in the least possible ethanol to form an

isotropic solution with the resulting water, as shown by the equation:



Each of 4-(dimethylamino) benzaldehyde was mixed with the primary aromatic amine in a volumetric flask (100 ml) and the mixture was dissolved with a small amount of ethanol, then the escalation of the reactant mixture began for two and a half hours, and then the product was filtered while it was hot after removing the boiling stone. Then it is cooled and filtered and the precipitate is taken and a recrystallization process is performed on it to get rid of impurities and to obtain pure crystals. The mentioned process is done with an appropriate solvent (Al-Wundawi , Ahmed Qassem , 2020). Then appropriate weights are taken from each of the prepared compounds (Schiff bases) to prepare (10-3M) by transferring them to a beaker and dissolving each of them with ethanol, then transferring to a volumetric vial with a capacity of (200) ml and completing the volume to the mark and then using it in preparing complexes Colored azo and set stability constants and optimal conditions as in the following table, which shows the symbols, names, structural formulas and molecular weights of the prepared Schiff bases:

### 4-Preparation of the diazotized reagent solutions (DDNA):

(0.549 g) of dinitro aniline is taken and dissolved in a beaker containing (50 ml) of acetonitrile and the solution is placed in a volumetric flask with a capacity of (100 ml) and the volume is completed with distilled water up to the mark so that the solvent ratio becomes (1:1) of acetonitrile and distilled water and kept in a cool dark place, using the instant nitrogen method. (Topwe Milongwe Mwene-Mbeja , 2019), and was applied spontaneously each time.

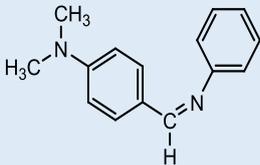
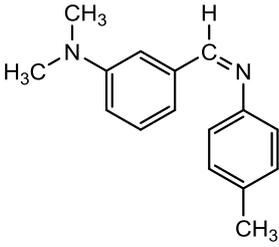
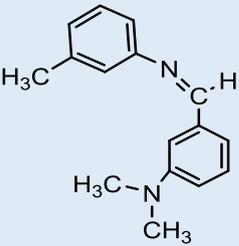
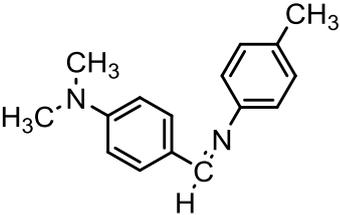
### 5-Preparation of (0.1M) sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) solution:

About (6.0 g) of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) is taken and placed in an electric oven at a temperature of (110-140°C) and the material is dried well, then cooled to laboratory temperature by placing it in a desiccator for at least half an hour, then weighed (5.3 g) of the dry matter, placed in a beaker and dissolved in a small amount of distilled water, then transferred to a volumetric bottle (500 ml) and the volume is completed to the mark with distilled water, thus

obtaining a standard solution of sodium carbonate with a concentration of (0.1M). Then weigh (2.65 g) of dry sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) in distilled water into a (500 ml) volumetric vial and supplement the volume to the mark with distilled water to obtain a standard solution of (0.1N) sodium carbonate. These solutions were used to control (16) the acidic function of the produced compounds at the required values (pH5, pH7 and pH9). Experimentally, different volumes of

sodium carbonate solution were added to the reagent and Schiff base solutions until the required acidity (pH) was obtained, because it was expected that a portion of the carbonate salt ( $\text{Na}_2\text{CO}_3$ ) would convert to carbonic acid due to the presence of hydrochloric acid (HCl) with the reagents solution. Thus, a mixture of weak carbonic acid and its salt is created, which acts as a buffer solution to adjust the pH.

Table(1): Symbols, names, structures and molecular weights of the prepared Schiff bases

Comp. No.	Symbol of 4-DMAB Derivative	Name	Structure	M. Wt.
1	4-DMABA	4-(Dimethylamino) Benzylidene Aniline		224.3
2	4-DMAB-o-T	4-(Dimethylamino) Benzylidene-o-Toluidine		238.3
3	4-DMAB-m-T	4-(Dimethylamino) Benzylidene-m-Toluidine		238.3
4	4-DMAB-p-T	4-(Dimethylamino) Benzylidene-p-Toluidine		238.3

### 6-Preparation of aromatic imine complexes solutions:

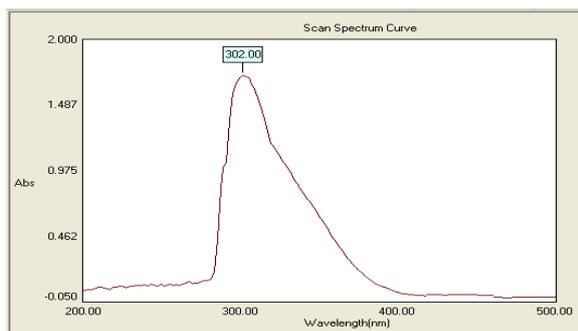
The aqueous solutions of the four imine complexes were prepared under optimal conditions previously obtained, by mixing appropriate quantities of (10-3M) from the diazotized reagent and (0.1M) from the carbonate salt ( $\text{Na}_2\text{CO}_3$ ) with (0.2ml) from (10-3M) from the Schiff base solution at a five

temperatures to obtain the required acidic functions : (pH5, pH7 and pH9).

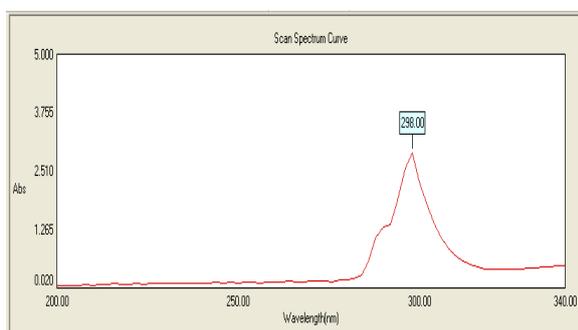
### Results and Discussion

The development in scientific research in all areas of life, including chemistry, led to an in-depth study and preparation of many types of complexes of great importance in medical, industrial and biological terms,

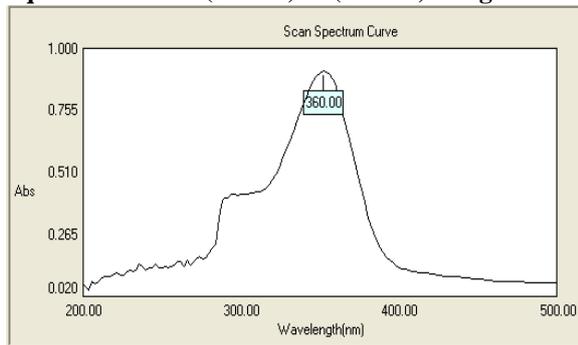




**Figure(1): Absorbance spectrum (UV-Vis.) for aqueous solution (10-3M) of Schiff base (4-DMAB-p-T).**



**Figure(2): Absorbance spectrum (UV-Vis.) for aqueous solution (10-3M) of (DDNA) Reagent.**



**Figure(3): Absorbance spectrum (UV-Vis.) for aqueous solution (10-3M) of(4-DMAB-p-T-DDNA) Complex.**

The following table (3) shows the wavelengths in nanometers for the reactants and products measured with an electronic spectrometer (UV ana Visible).

From table (3), we can conclude the following:

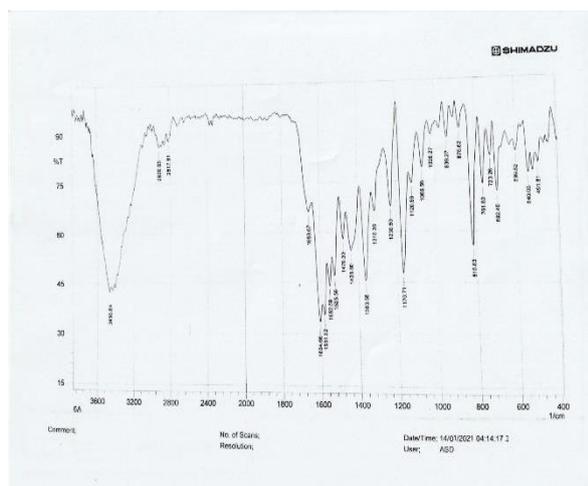
- 1- From the values of wavelengths ( $\lambda_{\max}$ ) obtained for the complexes and solutions of Schiff bases and for the reagent, it is clear that there is no interference between them, as well as the emergence of new bands for complexes that differ from the bands of the prepared Schiff base solutions and the reagent band.
- 2- The appearance of the resulting azo complexes in colors that differ from the colors of the Schiff bases under study is another evidence of the formation of new complexes resulting from the interaction of Schiff bases with the diazotized dinitroaniline reagent.

#### Identification of prepared compounds by (IR)(George Socrates, 2001):

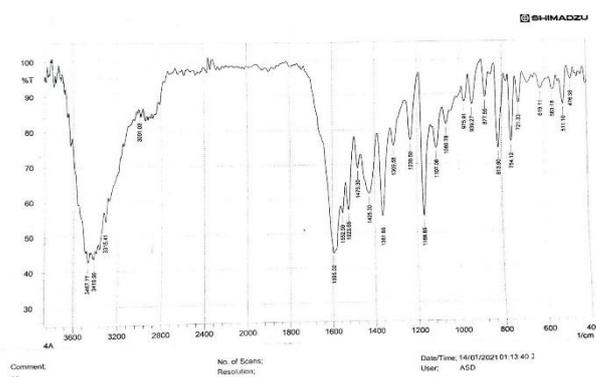
All the IR spectroscopic measurements of all the prepared compounds were measured in the solid state, as shown in the following figures for the IR spectra, starting with the basic compound with aniline (4-DMAB-An).

**Table (3): The obtained wavelengths of the reactants and products are measured by an electronic spectrophotometer (UV ana Visible).**

No.	The Symbol	$\lambda_{\max}$ (nm.) for Schiff base	$\lambda_{\max}$ (nm.) for Azo compound	Abs. of Azo Complex	$\lambda_{\max}$ (nm.) for (DDNA) Reagent
1	4-DMAB-An	314	344	2.022	302
2	4-DMAB-o-T	282	362	0.809	
3	4-DMAB-m-T	280	356	1.015	
4	4-DMAB-p-T	290	360	0.936	



Figure(4): IR spectrum of the compound (4-DMAB-p-T) in the solid state.



Figure(5): IR spectrum of the compound (4-DMAB-o-T) in the solid state.

All the bands obtained from the infrared spectrum (IR) of all the prepared compounds were tabulated to ensure their identification as in the following table:

Table(4): Spectral bands obtained from the infrared spectrum (IR) of all the prepared compounds.

No.	Symbol of comp. Derivatives	$\nu$ c=O	$\nu$ c-o	$\nu$ C=N	$\nu$ ph	$\nu$ NO <sub>2</sub>	$\nu$ OH FREE	$\nu$ Hb
1	4-DMAB-An	-	1479.30 1438.8	1604.66				3346.84
2	4-DMAB-o-T		1425.30	1595.02	1552.54 1523.66			3315.41
3	4-DMAB-m-T		1425.3 1477.37	1606.59	1577.66			3263.33
4	4-DMAB-p-T		1433.01 1498.59	1614.31	1567.31			3346.27

#### Study of the optimum conditions for the prepared azoimine complexes:

After the four complexes under study were diagnosed by several methods, including chemical and physical ones available in our laboratories. The time has come to study the optimum conditions for the formation of complexes of azo dyes after reacting the prepared Schiff bases with the diazotized dinitro aniline (DDNA) reagent, which is fresh azotization at a temperature of (273-278°K).

The most important optimal conditions are:

- 1-The optimum wavelength ( $\lambda_{max}$ ).
- 2-The optimum volume for the used reagent (DDNA).

3-The optimum volume of ( $\text{Na}_2\text{CO}_3$ ).

4-The optimum order of addition.

5-The optimum appearance time for the complexes formed was zero minutes in the complexes studied.

6-The optimum stability time for the formed complexes.

7-The optimum temperature for the formation of complexes.

The optimum conditions for each azo-imine dye formed by the reaction of the prepared imines with the diazotized reagent (DDNA) at certain pH and temperature (283°K) were studied and carefully tabulated to avoid repetition in speech, as in the following table (5):

Table (5): Optimum conditions for the four azo-imine dyes produced at certain pH and temperature (283°K).

No. of Complex	Symbol of Complex	Optimum Order of Addition	Optimum Wavelength (nm.)	appearance time(min)	stability time(min)
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1	4-DMAB-An	pH7.6	$0.2D + 1.5R + 0.2B$	344	0	35
		pH9.2	$0.25B + 1.5R + 0.2D$	338	0	40
2	4-DMAB-o-T	pH5	$0.4D + 0.3B + 0.4R$	362	0	20
		pH7	$0.4R + 0.5B + 0.4D$	358	0	45
		pH9	$0.4D + 0.9B + 0.4R$	356	0	35
3	4-DMAB-m-T	pH5	$0.3B + 0.4R + 0.2D$	356	0	30
		pH7	$0.6B + 0.2D + 0.4R$	352	0	35
		pH9	$0.9B + 0.2D + 0.4R$	348	0	65
4	4-DMAB-p-T	pH5	$0.2R + 0.2D + 0.4B$	368	0	35
		pH7	$0.2R + 0.6B + 0.2D$	362	0	50
		pH9	<b><math>0.2R + 0.9B + 0.2D</math></b>	356	0	40

Through table(5) the following is noted:

- 1- The structural form and the acidic functions (pH) are the most important factors in determining the optimal conditions and consequently the order of addition. This is in agreement with previous studies (Azzouz A. S. B. & Agha A. N. , 2005) and (Al-Niemi Mohammad Mahmoud , 2005).
- 2- The wavelength ( $\lambda_{max}$ ) in solutions with an acidic medium is higher than that of the same compound at a neutral or basic medium for most azo compounds, and the reason is due to the partial protonation that occurs in the azo dye complex or the formation of the nitrillium ion in the acidic medium, which is stable by resonance, which gives ease Due to the movement of electrons in the complex and thus the absorption energy of the complex decreases, and also due to the implicit hydrogen bond in the complex that forms an additional stable hexagonal ring for azo dye complexes (Azzouz A. S. B. et al.; 1995) and (Azzouz and Al-Niemi Mohammad Mahmoud , 2005).

#### Finding the ratios of the components (Stoichiometric ratio) for complexes:

Several studies, including (Azzouz A. S. B. & Agha A. N. , 2005) have confirmed that the photometric method includes in its aspects (3) different methods, namely the Job method, the molar ratio and the slope ratio method. Other studies (Joseph S. Renny et al. , 2013) showed that the molar ratio method is more Common among those methods because they can be applied to different systems, and the molar ratio method was adopted in our study.

When drawing a graphic relationship between the absorbance against the molar ratio (of the reagent/imine) a direct relationship is produced between them for all the resulting complexes at a constant temperature (283K). This relationship continues for the four compounds under study at certain acidic functions until reaching the maximum values that represent the ratios of the components of the process complex. It is also noticed after that the transformation of the relationship referred to above into an inverse relationship or the occurrence of some kind of negative deviation. And the following table (6) shows the mole ratios of the four donors prepared with the reagent (DDNA) at certain acid functions and at a temperature of (283K).

**Table(6): The mole ratios of the four donors prepared with the reagent (DDNA) at certain (pH) and at a temperature of (283K).**

No.	The Donor	pH	The mole ratios
1	4 – DMAB – An	7.6	<b>0.8</b>
		9.2	<b>0.5</b>
2	4-DMAB-o-T	5	<b>1.2</b>
		7	<b>1.2</b>
		9	<b>1.4</b>
3	4-DMAB-m-T	5	<b>1.2</b>
		7	<b>1.2</b>
		9	<b>1.2</b>
4	4-DMAB-p-T	5	<b>1.2</b>
		7	<b>1</b>
		9	<b>1.2</b>

From the previous table (6), we note that the molar ratios of all the prepared compounds are confined between (0.5-1.4), and this means that the mole ratios of all the prepared compounds are (1:1) in all the specific acidic functions (pH), and this is consistent with a previous study (Mokhtar Mabrouk , 2018).

#### Calculation of the stability constants for the prepared azoimine complexes:

The stability constants of the compounds resulting from the reaction of the four prepared imines with (DDNA) reagent were calculated at different pH functions and temperatures (273, 283, 293, 303 and 313oK). The obtained results are tabulated as in Table (7). whereas:

Es= absorption of a solution of the resulting compound containing stoichiometric ratios of reagent

and imine (Schiff's base) prepared. Under these conditions, the formed azo compound is relatively dissociated, with little absorption (Es).

Em= absorption of a solution of the resulting compound containing excess of the reagent, under optimal conditions. The solution is prepared in the same way as the first solution and is similar to it, but it contains an excess of reagent and at optimal conditions according to the table (Optimal Conditions). Here the resulting compound is more stable and the absorbance value is higher (Em).

After that, we find the product of (Em-Es)/Em for each studied solution against the blank solution in order to find the value( $\alpha$ ) from which the stability constant (K) is calculated, as follows:  $K=(1-\alpha)/(\alpha^2.C)$ .

**Table (7):The values of the stability constants for all aromatic azoimine complexes in different (pH) and temperatures prepared according to the optimal conditions and at their stability times.**

No.	Symbol of Azo imine compounds	pH	T(°K)	Es	Em	$\alpha$	K
1	4-DMAB+An	7.6	273	0.891	1.309	0.31933	333760
			283	0.571	0.882	0.35261	260348
			293	0.697	1.085	0.3576	251171
			303	0.567	0.928	0.38901	201877
			313	0.503	0.906	0.44481	140299
		9.2	273	0.815	1.053	0.22602	757534
			283	0.608	0.828	0.2657	520066
			293	0.592	0.903	0.34441	276350
			303	0.584	0.912	0.35965	247531
			313	0.579	0.946	0.38795	203333

<b>2</b>	4-DMAB+o-T	5	273	0.155	0.249	0.37751	218396		
			283	0.11	0.204	0.46078	126981		
			293	0.138	0.305	0.54754	75459.9		
			303	0.704	1.629	0.56783	67016.3		
			313	0.289	0.997	0.71013	28740.6		
		7	273	0.145	0.248	0.41532	169479		
			283	0.202	0.419	0.5179	89870.2		
			293	0.213	0.493	0.56795	66970		
			303	0.341	0.817	0.58262	61479.8		
			313	0.304	0.949	0.67966	34672.9		
		9	273	0.112	0.219	0.48858	107119		
			283	0.1829	0.441	0.58526	60540.5		
			293	0.147	0.376	0.60904	52699.2		
			303	0.708	1.992	0.64458	42772.3		
			313	0.203	0.789	0.74271	23321		
		<b>3</b>	4-DMAB+m-T	5	273	0.166	0.249	0.33333	300000
					283	0.128	0.204	0.37255	226039
					293	0.175	0.309	0.43366	150576
					303	0.512	1.062	0.51789	89875
					313	0.491	1.033	0.52469	86328.3
7	273			0.154	0.248	0.37903	216116		
	283			0.129	0.219	0.41096	174389		
	293			0.133	0.289	0.53979	78971.5		
	303			0.509	1.203	0.57689	63567.4		
	313			0.391	0.994	0.60664	53443.9		
9	273			0.149	0.218	0.31651	341126		
	283			0.14	0.22	0.36364	240625		
	293			0.131	0.217	0.39631	192178		
	303			0.903	1.991	0.54646	75940.1		
	313			0.302	0.732	0.58743	59779.3		
<b>4</b>	4-DMAB+p-T			5	273	0.556	0.776	0.28351	445719
					283	0.506	0.796	0.36432	239463
					293	0.448	0.761	0.4113	173998
					303	0.518	0.917	0.43511	149184
					313	0.377	0.739	0.48985	106301
		7	273	0.665	0.793	0.16141	1609329		
			283	0.507	0.665	0.23759	675282		
			293	0.505	0.684	0.2617	539028		

		303	1.014	1.566	0.35249	260568
		313	0.605	0.986	0.38641	205472
		273	1.188	1.439	0.17443	1356750
		283	0.541	0.709	0.23695	679509
	9	293	1.122	1.581	0.29032	420988
		303	1.111	1.593	0.30257	380895
		313	1.011	1.591	0.36455	239076

From Table (7), we conclude the following:

- 1- The values of the stability constants of the azo-imine dye compound generally decrease with increasing temperatures. This is consistent with the increasing degree of dissociation ( $\alpha$ ).
- 2- The values of the stability constants for the azo-imine dye compound formed vary according to the values of the acid functions. The reason is due to the fact that the electron pairs present on the active groups in Schiff bases are more likely to share with the reagent (DDNA) in the base medium than the acidic medium, and that the presence of these compounds in the medium works to restrict the electronegative pairs in the active groups, thus becoming less amenable to electronic donating and thus be weaker Lewis base.
- 3- Five different values of stability constants appeared for the azoimine dye compound formed at five different temperatures and for all the azo compounds formed. This means that these complexes are stable at change

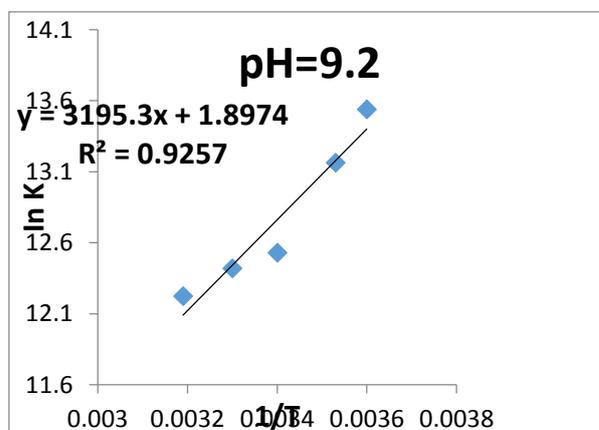
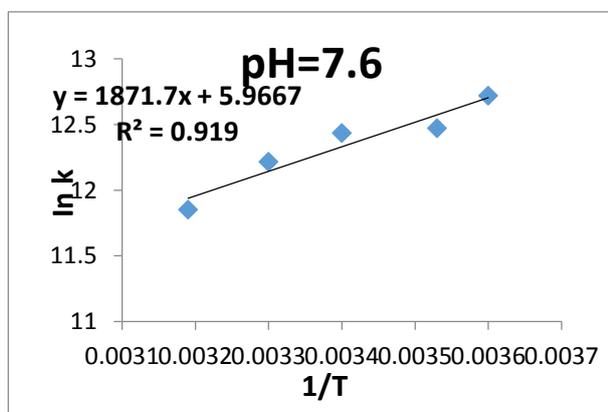
( $\Delta S^\circ$ ) were calculated from the mathematical relationship ( $\Delta S^\circ = (\Delta H - \Delta G^\circ)/T$ ). It was negative for all the resulting compounds and at all five temperatures.

- 4- The difference in the values of the stability constants for the formed four azo-imine dye compounds at the same temperature and at the same acid function is evidence of the effect of the structure of Schiff base on the values of the stability constants.

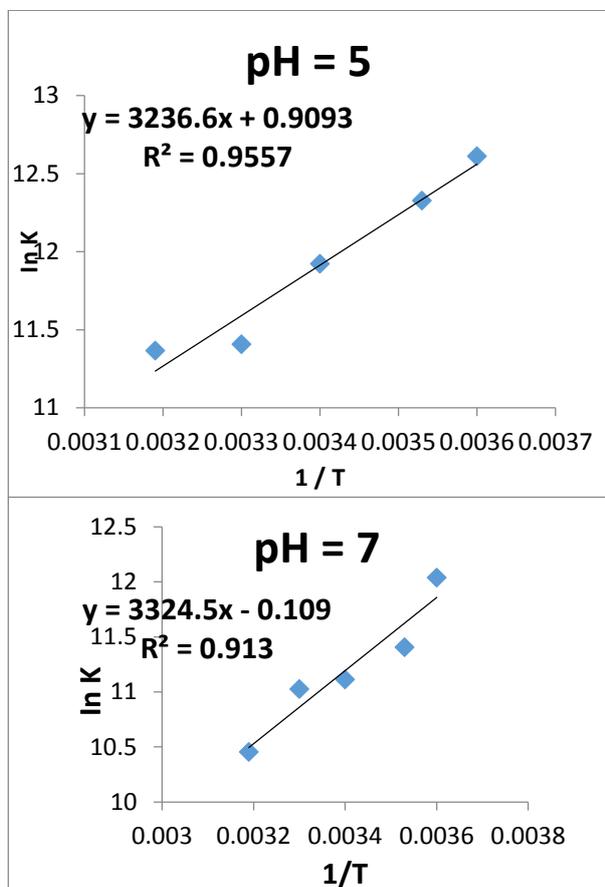
#### Thermodynamic study for the prepared azoimine complexes:

The stability study of all four azo-imine compounds formed at the optimal conditions for each of them, at different temperatures with a range of (273-313°K) and at different acid functions (pH), we were able to find the thermodynamic parameters for their formation.

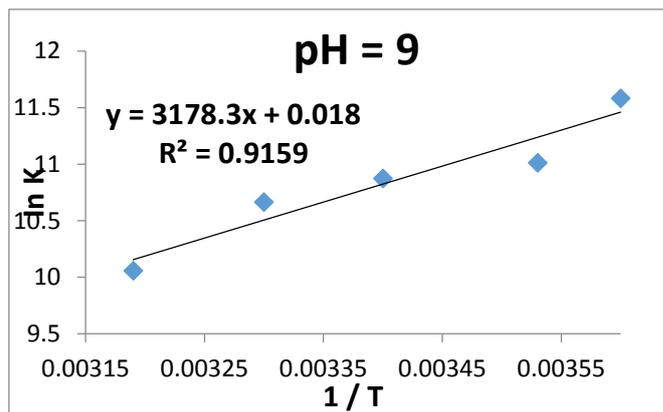
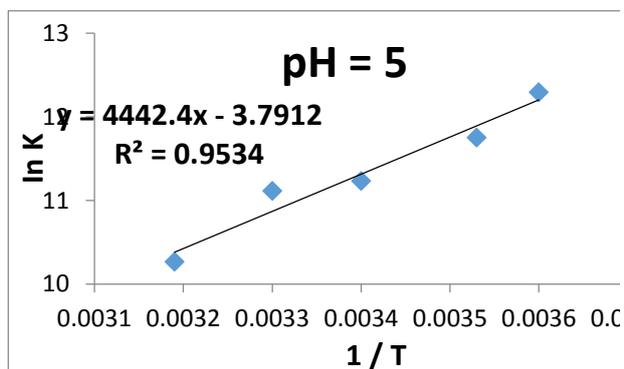
This study showed the effect of temperature on the values of the stability constants of the azo-imine compounds formed through the direct relationship obtained from the graph between ( $\ln K$ ) against ( $1/T$ ), so we obtained the following graphs (6-9):



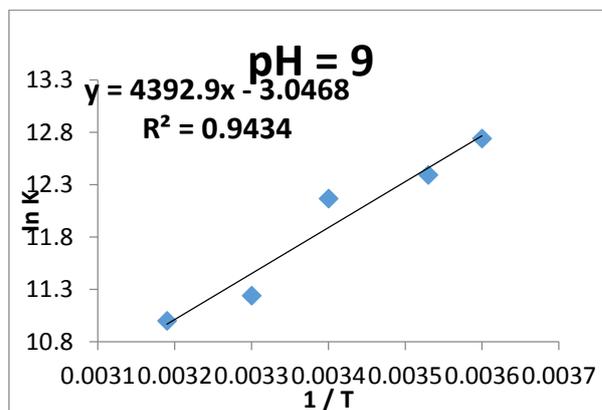
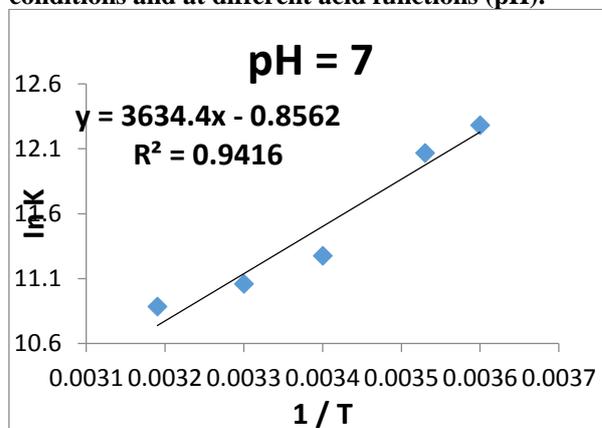
**Figure (6):** The effect of absolute temperatures on the stability constants of the azo-imine compound formed (4-DMAB-An+DDNA) under optimal conditions and at different acid functions (pH).

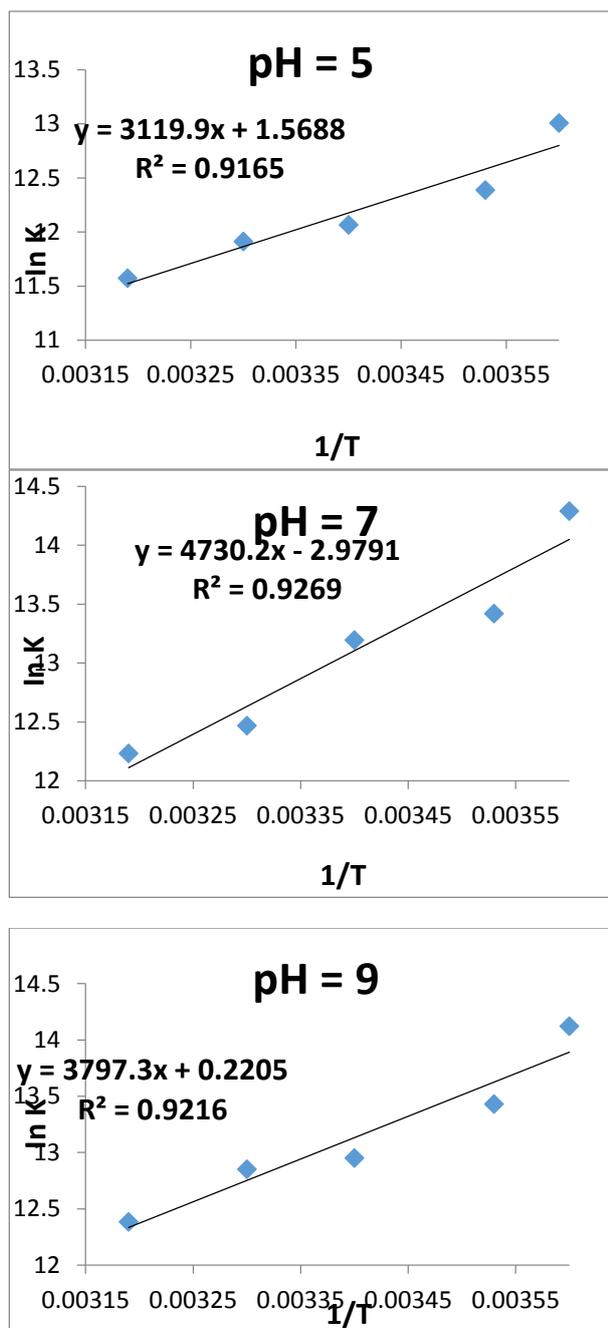


**Figure (7):** The effect of absolute temperatures on the stability constants of the azo-imine compound formed (4-DMAB-o-T+DDNA) under optimal conditions and at different acid functions (pH).



**Figure (8):** The effect of absolute temperatures on the stability constants of the azo-imine compound formed (4-DMAB-m-T+DDNA) under optimal conditions and at different acid functions (pH).





**Figure (9):** The effect of absolute temperatures on the stability constants of the azo-imine compound formed (4-DMAB-p-T-DDNA) under optimal conditions and at different acid functions (pH).

From the figures above:

- 1- The values of enthalpy change ( $\Delta H$ ) were calculated from the mathematical relationship ( $\Delta H = -R \cdot \text{Slope}$ ). It was negative for all the resulting compounds and at all temperatures and pH functions. These negative values indicate that these formation reactions are spontaneous towards the products.
- 2- The values of change in the standard Gibbs free energy ( $\Delta G^\circ$ ) were calculated from the mathematical relationship ( $\Delta G^\circ = -RT \ln K$ ) (Hari Dass N. D., 2014). It was negative for all the resulting compounds and at all temperatures and pH functions. These negative values indicate that these formation reactions are spontaneous towards the products.
- 3- The values of standard entropy change ( $\Delta S^\circ$ ) were calculated from the mathematical relationship ( $\Delta S^\circ = (\Delta H - \Delta G^\circ)/T$ ). It was negative for all the resulting compounds and at all temperatures and pH functions. These negative values indicate that these formation reactions reduce the randomness of the products.
- 4- The calculations mentioned above have been tabulated in the following table (8), which gives a summary of the thermodynamic study of the four resulting compounds at all temperatures and pH functions.

**Table (8):** A summary of the thermodynamic study of the four resulting compounds at all temperatures and pH functions.

No.	Symbol of Azo complexes	pH	T(°K)	ln k	$\Delta H$ (KJ.Mol <sup>-1</sup> )	$\Delta G^\circ$ (KJ.Mol <sup>-1</sup> )	$\Delta S^\circ$ (J.Mol <sup>-1</sup> )	$\Delta H_{AV.}$ (KJ.Mol <sup>-1</sup> )	$\Delta G^\circ_{AV.}$ (KJ.Mol <sup>-1</sup> )	$\Delta S^\circ_{AV.}$ (J.Mol <sup>-1</sup> )
1	4-DMAB+An	7.6	273	12.7182	-15.561	-28.867	0.04874	-15.561	-30.022	0.04934
			283	12.4698	-15.561	-29.34	0.04869			
			293	12.4339	-15.561	-30.289	0.05027			

		9.2	303	12.215 4	-15.561	-30.772	0.0502	-26.566	-31.062	0.0153 2
			313	11.851 5	-15.561	-30.841	0.0488 2			
			273	13.537 8	-26.566	-30.727	0.0152 4			
			283	13.161 7	-26.566	-30.968	0.0155 5			
			293	12.529 4	-26.566	-30.522	0.0135			
			303	12.419 3	-26.566	-31.286	0.0155 8			
			313	12.222 6	-26.566	-31.807	0.0167 4			
2	4- DMAB+ o-T	5	273	12.294 1	-36.934	-27.904	-0.0331	-36.934	-27.525	-0.0321
			283	11.751 8	-36.934	-27.65	-0.0328			
			293	11.231 4	-36.934	-27.36	-0.0327			
			303	11.112 7	-36.934	-27.994	-0.0295			
			313	10.266 1	-36.934	-26.715	-0.0326			
		7	273	12.040 5	-27.64	-27.329	-0.0011	-27.64	-27.243	-0.0014
			283	11.406 1	-27.64	-26.837	-0.0028			
			293	11.112	-27.64	-27.069	-0.0019			
			303	11.026 5	-27.64	-27.777	0.0004 5			
			313	10.453 7	-27.64	-27.204	-0.0014			
		9	273	11.581 7	-26.424	-26.287	-0.0005	-26.424	-26.343	-0.0003
			283	11.011 1	-26.424	-25.908	-0.0018			
			293	10.872 4	-26.424	-26.485	0.0002 1			
			303	10.663 6	-26.424	-26.863	0.0014 5			
			313	10.057 1	-26.424	-26.171	-0.0008			
3	4- DMAB+ m-T	5	273	12.611 5	-26.909	-28.625	0.0062 8	-26.909	-28.997	0.0071 1
			283	12.328 5	-26.909	-29.007	0.0074 1			
			293	11.922 2	-26.909	-29.043	0.0072 8			
			303	11.406 2	-26.909	-28.734	0.0060 2			
			313	11.365 9	-26.909	-29.577	0.0085 2			
		7	273	12.283 6	-30.216	-27.88	-0.0086	-30.216	-27.988	-0.0076

4	4-DMAB+ p-T		283	12.069	-30.216	-28.397	-0.0064			
			293	11.276 8	-30.216	-27.47	-0.0094			
			303	11.059 9	-30.216	-27.861	-0.0078			
			313	10.886 4	-30.216	-28.329	-0.006			
		9	273	12.74	-36.523	-28.916	-0.0279	-36.523	-28.928	-0.0259
			283	12.391	-36.523	-29.154	-0.026			
			293	12.166 2	-36.523	-29.637	-0.0235			
			303	11.237 7	-36.523	-28.309	-0.0271			
			313	10.998 4	-36.523	-28.621	-0.0252			
		5	273	13.007 4	-25.939	-29.523	0.0131 3	-25.939	-29.638	0.0126 1
			283	12.386 2	-25.939	-29.143	0.0113 2			
			293	12.066 8	-25.939	-29.395	0.0117 9			
			303	11.912 9	-25.939	-30.01	0.0134 4			
			313	11.574	-25.939	-30.119	0.0133 5			
		7	273	14.291 3	-39.327	-32.437	-0.0252	-39.327	-31.884	-0.0254
			283	13.422 9	-39.327	-31.582	-0.0274			
			293	13.197 5	-39.327	-32.149	-0.0245			
			303	12.470 6	-39.327	-31.415	-0.0261			
			313	12.233 1	-39.327	-31.834	-0.0239			
9	273	14.120 6	-31.571	-32.05	0.0017 5	-31.571	-31.959	0.0013		
	283	13.429 1	-31.571	-31.597	9.2E-05					
	293	12.950 4	-31.571	-31.547	-8E-05					
	303	12.850 3	-31.571	-32.372	0.0026 4					
	313	12.384 5	-31.571	-32.228	0.0021					

From Table (8), we conclude the following:

**1-** Negative ( $\Delta H$ ) and ( $\Delta H_{av.}$ ) values, which gave stability constants for the four azoimine compounds produced at all five temperatures and at the acidic functions shown, indicating that the formation reactions of azoimine compounds are exothermic reactions.

**2-** The values of ( $\Delta G^\circ$ ) and ( $\Delta G_{av.}^\circ$ ) for the above-mentioned reactions were also negative for the four azoimine compounds produced at all five temperatures and at the acid functions shown. This indicates that the reaction of its formation is a spontaneous reaction.

- 3- As for the values of the change in entropy ( $\Delta S^\circ$ ), they should be negative in theory. This is consistent with most of the studied compounds at certain acidic functions. As for the compounds that gave positive ( $\Delta S^\circ$ ) values, the reason is attributed to the action of the hydrogen bond in these complexes whose strength and energy are affected by temperature change, in other words, the hydrogen bonds transform change values of ( $\Delta S^\circ$ ) to the positive sign.
- 4- The different values of ( $\Delta S^\circ$ ,  $\Delta G^\circ$ ,  $\Delta H$ ) when the resulting compound differs is believed to be caused by the structures of the studied complexes. This is consistent with a lot of studies (Elena P. Salvador, 2012).

#### The effect of the acid function (pH) on the stability constants of the prepared imine compounds:

The tautomerism of Schiff bases is greatly affected by the change of the pH function (Azzouz et al., 2005) and the compounds that were prepared at the beginning of our study are imines of various shapes. For this reason, we have studied these imines at different acid functions and at different absolute temperatures. This shows five different values of stability constants for all the azo compounds formed. This means that these complexes are stable at these five temperatures.

It is worth noting in Table (8) that the complexes in the basic medium (pH9) are relatively more stable than in the acidic medium (pH5). The reason is due to the fact that the electronegative pairs present on the active groups in Schiff bases are more likely to be shared with the reagent (DDNA) in the base medium than in the acidic medium. And that the presence of these compounds in the medium works to restrict the electronic pairs in the effective groups and become less amenable to electronic grants and thus be weaker as the Lewis base.

#### The effect of the structures of the prepared imine compounds on the stability constants:

Changing in the structures and substitutes for the compounds studied in this research is one of the factors that directly affect the chemical reactions. The difference in the values of the stability constants for the formed four azo-imine dye compounds at the same temperature and at the same acid function is evidence of the effect of the structure of Schiff base on the values of the stability constants. The substitutes affect

the stability constants (Azzouz & Al-Dilami, 2005) of the prepared azoimine compounds in addition to their effect on their electronic spectra.

This is consistent with the literatures (Batsanov, Stepan S. , et al., 2012).

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