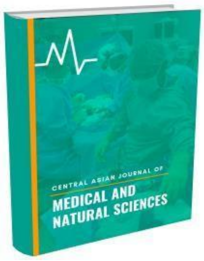

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Article

Research Entitled (Spectroscopic And Thermodynamic Study Of A Number Of Charge Transfer Complexes Derived From The Reaction Of 3-Methoxy-4-Hydroxybenzaldehyde And A Number Of Aromatic Amines With A Number Of Electronic Receptors

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Abstract: Nine of the lipid bases derived from 3-methoxy-4 hydroxy-benzaldehyde and some aromatic amines, such as aniline and aniline compensated with (2-hydroxy, 4-hydroxy, 2-amino, carboxy, 4-), nitro-phenol and tri-nitro phenol (weak acid) in the solvent ethanol by using the radial spectrum Ultraviolet. The Pensi-Hildebrand equation was used by following the length of the upper wave of the complex to calculate its equilibrium constant at concentrations of 1x10-4 (M: 1x10-5)

Keywords: Lipid Bases Synthesis, Ultraviolet Spectroscopy, Equilibrium Constant Calculation

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1. Introduction

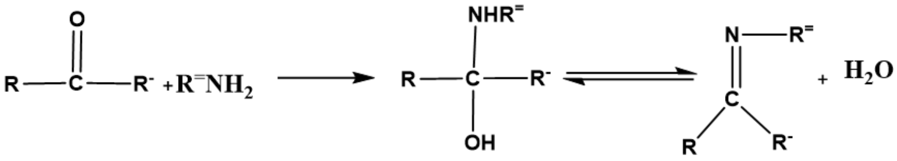
1.1 Summary of the Schiff base:

The Schiff base was defined as compounds with a functional group containing the active azomethine group (C=N) and the nitrogen atom binds to the aryl or alkyl group and not hydrogen and the general formula of the Schiff bases R1R2C = NR3 where the Rl is an aryl group, R2 = H, R3 alkyl or aryl [1,2].

The Schiff rule is defined as compounds that contain the azomethine group and some call it the second term dominate (azomethine when carbon binds to a hydrogen atom where the formula RCH=NR is from primary amine, aldehyde or ketone)

The R series associated with nitrogen that makes a stable Schiff base is Amine, and when the Schiff base derived from aniline, i.e. R3, is phenyl or vinyl compensated, we call the Schiff anilate bases [3-6].

The most common method for obtaining SHEF rules is the method of condensation reaction [7-9] between carbonyl compounds (I) and amine (II), where an intermediate state (III) is formed and then converted to the product, as shown in the following equations:



[I] [II] [III]

1.2. Devices used:

1. Measurement of electronic spectra:

A two-cell-type UV spectrometer was used (Cecil (UV – Visible) Spectrophotometer UV - CE 3021 (For spectroscopic measurements and use a single-cell spectrometer of type (Jenway spectrophptometer 6405 UV –visible) for thermodynamic and kinetic measurements using a quartz cell with dimensions (3x1x1) To measure models.

2. Infrared spectrometer:

The infrared spectra of all prepared SHV bases were recorded using a Shimadzo IR Affinity -1 device in the area between cm-1 (400-4000), using potassium bromide KBr as tablets.

3. Sensitive balance (four decimal places) :

Satorial BL 210S.

4. Melting Point Measuring Device:

The melting points of the prepared flange bases were measured using a device of the type Melting point tester Mettler FP 61 3.1 Chemicals used:

2. Materials and Methods

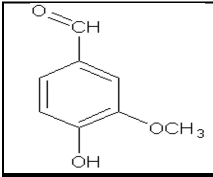
The methodology section of the research involves the preparation and analysis of Schiff bases. Specifically, the Schiff bases were prepared by mixing equimolar amounts of aldehydes and primary amines dissolved in ethanol. The mixtures were stirred at room temperature, leading to the formation of precipitates. These precipitates were then recrystallized using ethanol to purify them. After drying, the products were analyzed by measuring their melting points and recording their UV and infrared spectra to identify absorption bands. The study employed spectroscopic methods, including UV and infrared spectroscopy, to characterize the synthesized Schiff bases. These techniques helped determine the electronic structure and functional groups present in the compound

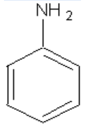
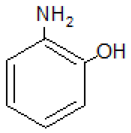
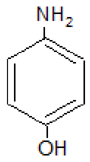
3. Results and Discussion

3.2. Amines and aldehydes :

The raw materials used in this research to prepare the lip bases shown in Table 1 are prepared by Merck Foundation and are of high purity and were used directly without additional purification except for aniline, which was distilled at 0C(187) in addition to the use of absolute ethanol as a solvent and ethanol 96% to study the kinetics of the decomposition of complexes.

Table 1:Chemicals used in the preparation of Schiff base and their physical properties.

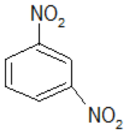
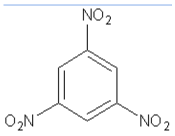
NO	Scientific name	Synthetic Formula	Melting Point	Color
1	**3-methoxy-4-hydroxy benzaldehyde**		**81**	**White**

2	**Aniline**		**Liquid b.p 183**	**colourless**
3	**2 -hydroxy aniline**		**225**	**White**
4	**4- hydroxy aniline**		**102**	**Dark Brown**

3.2. Receivers:

The following materials are prepared by the Merck Foundation:

Table 2:Receptors and their molecular structures used in research, wavelengths and colors in the absolute ethanol solvent.

NO	Scientific name	Icon	Synthetic Formula	λ (nm) ε_{max} (L.mol^{-1}.cm^{-1})	Color
1	Iodine	I	I_2	445	black
2	m-Dinitro benzene	DNB		224 324 357 (1487) (530) (510)	Light yellow
3	1,3,5,-tri nitro benzene	TNB		216 220 228 (1890) (2341) (2275)	Light Brown

3.3. Preparation of Schiff base :

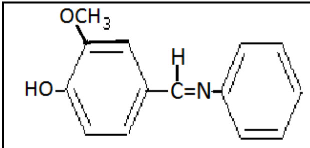
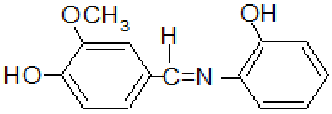
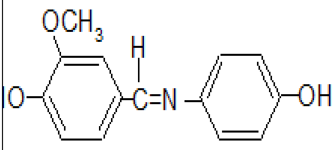
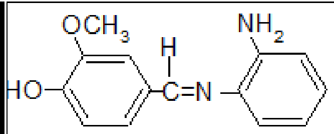
Schiff's rules were prepared in this research by mixing equivalent molar quantities of both aldehyde and primary amine after dissolving them with ethanol according to the methods known as literature (4.5) as follows:

3.3.1 The method of preparing Schiff base:

I dissolve (1.52, 0.01 gm mol) of aldehyde (3-methoxy-4-hydroxy benzaldehyde) in (10ml) of absolute ethanol and add (1.0 0.01, gm mol) of (2-hydroxy aniline) dissolved in (10ml) of absolute ethanol. Shake for (30-60) minutes using a magnetic stirrer mixer at a temperature The chamber to give a precipitate is recrystallized twice using absolute ethanol after drying the resulting precipitate, a yellowish-white precipitate was obtained, its melting point was measured and the ultraviolet and infrared spectrum were taken to determine its absorption beams.

Table 3:Names, shapes, and some physical properties of the rules of the prepared Schiff base

No. comp.	Syntactic formula and scientific name	degree Fusion	λnm Ɛ(L.mol^{-1}.cm^{-1})	Color

1	 3-methoxy – hydroxybenzyliden aniline	**158**	**227 (1772)** **285 (1837)** **32 (1192**	Light yellow
2	 3-methoxy -4-hydroxybenzyliden -2$^{\backslash}$-hydroxy aniline	**192**	**232 (1157)** **292 (1200)** **30 (1084**	**White Yellowish**
3	 3-methoxy -4-hydroxybenzyliden -4$^{\backslash}$-hydroxy aniline	**60**	**208 (1216)** **280 (1907)** **2 (1630**	**brown Bold**
4	 3-methoxy -4-hydroxybenzyliden -2$^{\backslash}$- amino aniline	**180**	**205 (1540)** **279 (1890)** **28 (147**	**brown-yellowish**

3.4.1. Electronic spectra of Schiff base:

The simplest uncompensated molecule of the ormatic Schiff bases (benzylidine-aniline) absorbs light at three known locations in UV spectroscopy [10,11]. Electronic spectra with ethanol solvent for SHF bases (1-4), the participation of these bases is observed in three absorption beams The locations of these beams change according to the change of molecular structure (according to the compensator on the aniline and benzaldehyde rings), the first beam: at values of (205, 208, 209, 214 nm) which represents the high-energy beam and represents the *π-π transition beam of the benzaldehyde ring, which is not a significant beam.

The second beam: at the values of (278, 279, 280, 285, 292) nm of bases and represents a beam with high energy high values of its molar absorption

coefficient (ε =1200-2426 L.mol-1.cm-1) It represents the charge transfer package for the azomethene group, in which the benzaldehyde ring is an electron donor and the azomethene group is an electron receptor, and it represents the local excitation package *π-π for the benzaldehyde ring, and this package is very important in changing its location with the compensators on the aniline ring affecting the azomethine group as a result of hydrogen bonding or mesomeric effect or resonance effect.

As for the third beam, which is very important and representative of electronic transmission as well, *π- π extended through all the molecule, whose origin is PhN = C, which appears at the values (304, 310, 328, 336, 372) nm, which is a beam with less energy (with less intensity) values of its molar absorption coefficient (ε= 1084-1630L.mol-1.cm-1) The last two beams are very important in determining the electronic form of the molecule and when comparing these beams of bases (1-4) with base beams (1) we find that the compensators on the aniline ring have affected so much that most of them showed a decrease in the location of the second and third beam (blue offset) except for a little All the molecules studied for Schiff bases have implicit or interfacial hydrogen bonds or both and the third beam is the charge transition pack as a result of the formation of the complex.

3.4. 2. Diagnosis of compounds (Schiff base):

Some physical and spectral properties were measured to diagnose the compounds of the prepared Schiff bases, as the melting points of these compounds were measured and showed a difference between them and their constituent materials and have relatively large intermolecular forces such as (hydrogen bond) and dipole-dipole attraction, which explains the high melting points Table 3 as well as these compounds were diagnosed using available spectral methods, as the compounds were diagnosed with infrared spectroscopy, as it shows the locations of the absorption beams belonging to the Schiff bases and the compounds that were prepared from them in the case Solid and Bent The area of functional aggregates The appearance and disappearance of some beams What distinguishes the infrared spectrum of the Schiff bases consisting of the primary amine and aldehyde is the disappearance of two beams, one of which is the vibrational beam belonging to the carbonyl group at the region (cm-1 1700) as well as the homologous and asymmetric beam belonging to the group (-NH2) belonging to the amine and the appearance of a strong beam at the region (cm-1 1600 - 1622) belonging to the azomethene group C = N and this gives a clear and strong evidence of the occurrence of the condensation process between aldehyde and amine and Table 4 shows the I.R spectrum For some of these compounds .

The elastication beam due to vibration of the C=N group is directly affected by the presence of compensators on the aniline ring and benzaldehyde, where the effects of resonance and induction are very clear to change the location of this beam as a result of changing its electronic density due to these two factors, as well as the emergence of other important beams in the diagnosis of compounds, but not important in the diagnosis of the Schiff base and its composition of its raw materials, namely beams (Ar-H, 2NO, C=C, C-X) And other beams that did not show a significant difference in their locations when these bases are formed compared to their location with the raw materials consisting of them, as well as the infrared spectra show the appearance of the vibration beam of the OH group at frequency (3324-3392) indicating the appearance of the hydraagent group is clear, the width of the beam indicates the implicit hydrogen adhesion between the hydrogen atom of the hydroxyl group at the ortho site on the aniline ring and the nitrogen atom of the azomethene group.

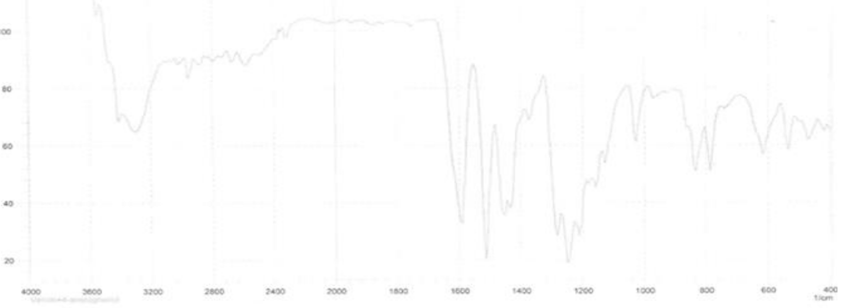


Figure 1: Infrared spectrum of the compound [M1]

Table 4:I.R. absorption packet values for prepared schiff bases

No. of comp.	$\upsilon_{C\text{-}HAr}$ cm^{-1}	υ C=N cm^{-1}	υ C=C cm^{-1}	υ_{OH} cm^{-1}	Other
1	3087 b	1622 s	1461 w	3392 b	
2	3065 w	1604 s	1499 b	3371 b	
3	3078 s	1600 s	1467 b	3324 w	
4	3303 b	1604 s	1511 w	3375 w	

s= sharp
b = broad
w =weak

3.4.3. Cargo transport complexes:

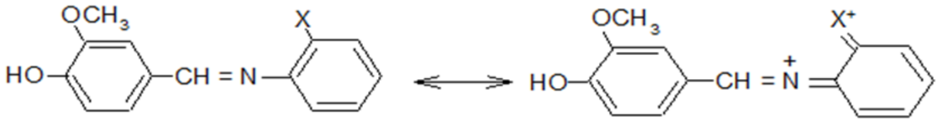
The four bases prepared from aldehyde (3-methoxy-4-hydroxybenzaldehyde) with some aromatic amines, were used as donor for electrons due to the abundance of electrons in their composition as well as the difference of compensators on them from propellant or pulling groups at the ortho or para site with electron-acceptor molecules in the ethanol solvent to verify that they are:

1. Charge transfer complexes with σ type iodine receptor.
2. Charge transfer complexes with non-acid receptors (DNB, TNB) of π type.

After measuring the wavelengths of the highest absorption of both bases and receivers in this study to ensure that there are no overlaps between their absorption beams with the absorption beams of complexes and to adopt the receiver as a reference in all measurements performed.

The higher absorption beams (λmax) of the complexes formed by mixing the donor solution (base) with the receptor solution in ethanol were monitored using UV spectroscopy and tables (1-3) show the physical properties of all charge transfer complexes.

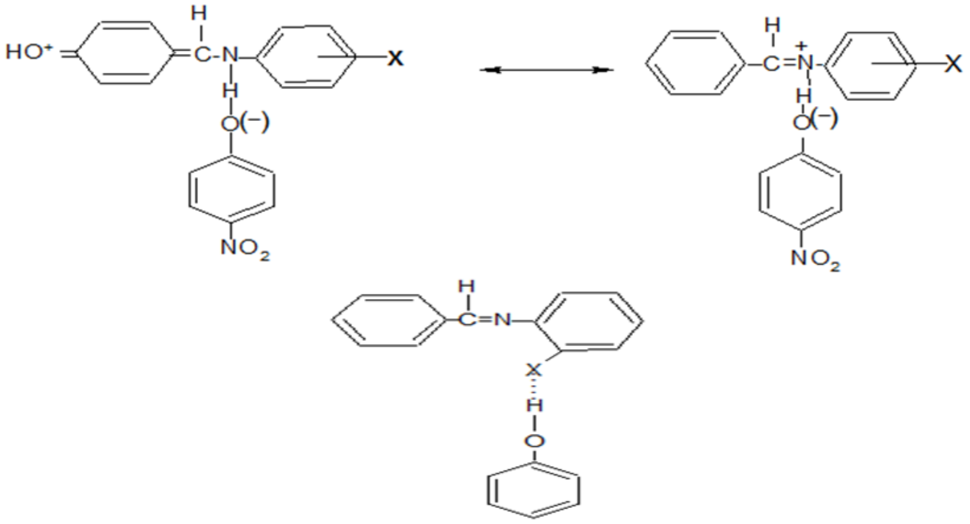
The absorption beams (λmax) For all charge transfer complexes appeared with a higher wavelength (new beams in the ultraviolet and visible regions), but (strongly) lower cards. When comparing the absorption beams of all complexes (1-4) with the single receptor with the absorption beam of the uncompensated base (1), a red shift is observed for all complexes, especially for the compensated complexes at the site Ortho of the aniline ring Helps in the possibility of a stable pentagram or hexagonal ring by the participation of an atom of hydrogen atom hydroxyl or amine group or nitro or carboxy group in a bond Implicit hydrogen with electron double or with the proton of a carbon atom of the azomethene group in addition to the vacuum impairment factor of these aggregates has a very important role (because they are located near the center of interference with the receiver) in weakening the interference force between the base and the receiver.



The ionization potential values of bases (1-9) are high with DNB, TNB, I2 receptors for being non- acidic and can gain an electron,

Figures 2 to 3 represent the application of the Bensi–Hildebrand equation for rules (1-4) with electronic receivers. From drawing the relationship between $\frac{AO}{O.DCT}$ versus $\frac{1}{[S.B]}$ the values of the equilibrium constant K_{CT} equal to Intercept/slop are calculated, and the K_{CT} value determines the strength of the formed complex, which is determined by the strength of the receiver, the strength of the base and the compensators on it in terms of their effect and presence relative to the center of interference with the receiver and the possibility of the receiver correlation with the base by compensated sums. An indication of the effect of the vacuum disability factor of the compensator and the size of a particle The future, which sometimes leads to a variation in the values of the equilibrium constant of the complexes, and this requires supporting the study in the future using known quantum mechanics methods to support and prove the values and interpret the results to unite all the clarifications, but the linearity of the strong relationship with the forms referred to above is inferred from the good correlation coefficient values (R2) that can be adopted in the Bensi-Hildebrand equation in calculating the values of the equilibrium constants shown in Table (3-8) with the receivers.

Most likely, the presence of the driving groups on the aniline ring at the site para of the azomethene group of complexes (5,3) makes them susceptible to the formation of charge transfer complexes stronger than the rest of the complexes compensated by pulling groups because it increases the base on the nitrogen atom of the azomethene group and thus helps the stability of the resulting complexes as shown by the values of the equilibrium constant of the substituted bases at the site para (5,3), which is almost twice its value for the rest of the other complexes. The density on a nitrogen atom of the azomethene group is larger, which leads to an increase in interference with the receptor, but the presence of these groups in the ortho site with some compounds makes the effect of vacuum obstruction a greater role, weakening the role of the mesomeric effect, so the interference decreases as a result of the lack of density on the nitrogen atom of the azomethine group due to vacuum obstruction, , the pulling or thrust force of the groups is affected by several factors, including the size of the molecule and its spatial arrangement (geometry) and its location of the influential group azomethene and others, as well as the joint effect by the compensators on the benzylene ring in which all complexes participated because it is from the same aldehyde and thus affected the values of the equilibrium constant, and this means that the formation of these complexes is the result of interference of these bases with receptors represented by the transfer of a charge from HOMO to the base molecule and represented by the empty orbital LUMO for the receptor molecule except for complexes : With iodine for orbital (*σ).



The presence of pulling groups on the aniline ring, whether at the ortho site or para of the azomethene group, leads to an increase in the electron density on the group itself (puller), which makes it more susceptible to interference with the solvent.

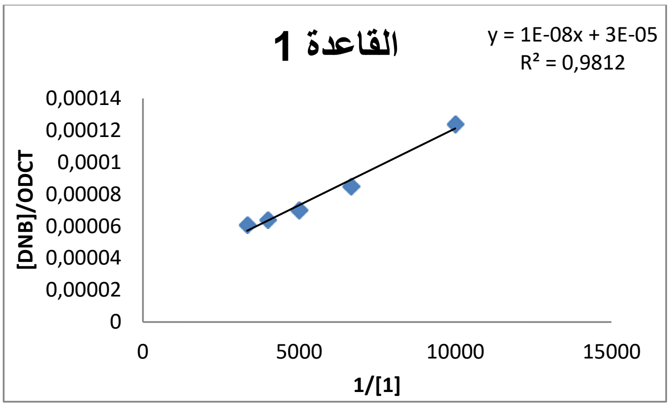


Figure 2: Application of the Penci-Hildebrand equation of Rule 1 with the DNB receptor in an ethanol solvent at room temperature

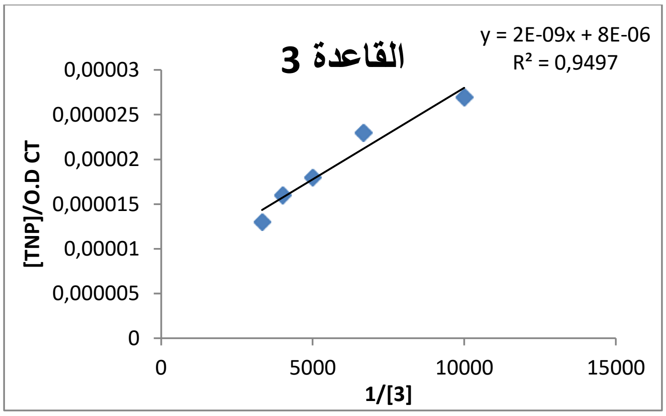


Figure 3: Application of the Penci-Hildebrand equation of base (3) with the TNB receiver in a solvent

Table 5: Equilibrium constant values K_{CT} and correlation coefficient R2 for bases (1-6) with receivers

S.B	I_2		DNB		TNB	
	K_{CT}	R^2	K_{CT}	R^2	K_{CT}	R^2
1	2500	0.9925	3000	0.9812	3500	0.9848
2	2250	0.9831	1000	0.9719	1000	0.9472
3	2666	0.9433	3333	0.9779	3750	0.9834
4	2000	0.9984	800	0.9885	833	0.9718

Table 6: Decay rate constant of SHF bases k and half-life t1/2 with TNB receiver, I2

S.B	I_2		TNB	
	$k(min^{-1})$	$t_{1/2}$ (h)	$k(min^{-1})$	$t_{1/2}$ (h)
1	0.0240	0.4	----	----
2	0.0018	6	----	----

3	-----	----	----	----
4	----	----	----	----

4. Conclusion

1. Schiff bases prepared from (1-9) electron donor compounds with different ionization potential with acceptors according to the following order: DNB > TNB > I2 TNP ≈ p-NP.
2. The solutions of these bases with acceptors are subject to the Pence-Hildebrand equation with a ratio of 1:1.
3. Calculating the stability constant (KCT) for the formed compounds which were affected by the type of substituent on the benzaldehyde and aniline rings of the base molecule and the hydrogen bond and the steric hindrance in the molecule. The equilibrium constant values for these compounds were in the following order:
   TNP > p-NP > TNB > DNB > I2
4. The bonding or interference between the base and the acceptor occurs either of the n-π* type or of the π-π type for all bases with acceptors except the iodine acceptor.

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