

Spectral and kinetic studies for some new β -diketo Schiff bases derived from 2-pivalloyl-1,3-indanedione

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Abstract :

New β -diketo Schiff bases have been prepared from condensations of 2-pivalloyl-1,3-indane dione with o-phenylene diamine and five substituted ortho- phenylene diamines and their structure were identified by IR, mass fragmentation and C.H.N analysis. The CT complexes of these Schiff bases (1-6) with three acceptors molecules(p-CA ,DDQ ,and TCNE) have been studies in CH_2Cl_2 solution . The electronic absorption spectra of these compounds (1-6) have been estimated under different polar solvents , and also the study included the dissociation kinetics of these Schiff bases under aqueous medium and acid condition. It was found that the rate determining step hydrolysis of these β -keto Schiff bases is first order kinetics and depended upon the nature of the substance on the amine rings .

Introduction

It is well known that β -keto Schiff bases were obtained from condensation of the β -ketone with appropriate amine.⁽¹⁻⁴⁾ The uv, ir and mass fragmentation of these compounds have been investigated previously.⁽⁵⁻⁹⁾ The charge-transfer complexes for these compounds with some acceptors were studied and the ionizations potential of these donors, physical parameters of some acceptors and CT complexes have been estimated^(10-16.) The dissociation kinetics of the Schiff bases and β -keto Schiff bases and CT complexes have been examined in neutral acidic and basic aqueous media and variable pH were also determined. The rate determining step hydrolysis was detected in the case of compound ⁽¹⁷⁻²³⁾. The aim of this work is to identify the structures of new(6) β,β -diketo Schiff bases derived from 2-pivalloyl-1,3-indane dione with different substituted

ortho phenylene diamines by ir, mass fragmentation and C.H.N analysis and study the CT complexes and solvent effects and the hydrolysis of these Schiff in different aqueous media

Materials and methods

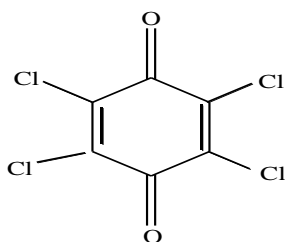
1- Chemical

A -Organic materials

2-Pivalloyl -1,3- indane dione (purity 98%), and O-phenylene diamine and derivative (4- substituted such as 4-OH, 4-Br ,4- NO_2 4- OCH_3 , ,and 4- COOH) .

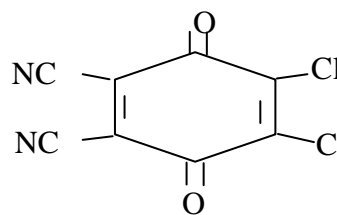
Acceptors; (1). 2,3,5,6, - tetra chloro - 1,4-benzoquinone (p-CA purity 95%): (2). 2,3-dichloro -5,6-dicyano-1,4-benzoquinone (DDQ purity97%) and(3) . Tetra cyano ethylene (TCNE) were of Fluka

(1)



P-CA (2,3,5,6-tetra chloro
1,4-benzoquione)(Yellow)

(2)



DDQ (2,3-dichloro-5,6-dicyano1,4- benzoquinone)
(Yellow)

B - Solvents

Ethanol (absolute), Methanol (Analar), Methylene Chlorid (98%) were of BDH, and dimethyl formamide (DMF) with Fluka .Concentrated Acid (HCl . H_2SO_4) and Acetic acid (Analar). All the chemicals are used without further purifications.

2- Experimental

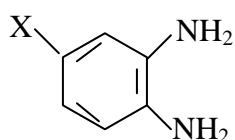
2-1 : Preparations of β , β -diketo Schiff bases:

Equimolar quantities of 2-pivalloyl 1,3-indane dione and the corresponding derivative of o-phenylene diamine

(Scheme 1) were refluxed for 30-45 minutes in absolute ethanol (10-25 ml).In case of (3,4,6) 10-15 drops of glacial acetic acid were added to the mixture, after cooling a solid product was separated .The solid in every case was washed repeatedly in boiling ethanol, the yield was in the range of 50-60% (Tables1,2) represents the β -keto Schiff bases ,melting point ,IR and C.H.N. analysis and the physical state of these compounds. the following β,β -diketo Schiff bases have been prepared in the following articles (Scheme 2)

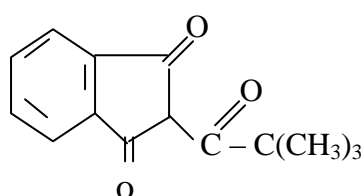
Table (1) : Some physical properties of β,β' -diketo Schiff bases.

No.S.B	Name	M. p /c°	Formula	M.Wt.	Physical state
1	2-Pivalloyl-1,3-indanedionylidene-2-amino aniline	>350	C ₂₀ H ₂₀ N ₂ O ₄	320	Green powder
2	2-Pivalloyl-1,3-indanedionylidene-4-hydroxy-2-amino aniline	222-224	C ₂₀ H ₂₀ N ₂ O ₃	337	Yellow
3	2-Pivalloyl-1,3-indanedionylidene-4-bromo-2-amino aniline	271-273	C ₂₀ H ₁₉ BrN ₂ O ₄	399	Yellow powder
4	2-Pivalloyl-1,3-indanedionylidene-4-nitro-2-amino aniline	180-182	C ₂₀ H ₁₉ N ₃ O ₄	365	Red
5	2-Pivalloyl-1,3-indanedionylidene-4-methoxy-2-amino aniline	237-239	C ₂₁ H ₂₂ N ₂ O ₃	350	Yellow
6	2-Pivalloyl-1,3-indanedionylidene-4-carboxy-2-amino aniline	278-280	C ₂₁ H ₂₀ N ₂ O ₄	364	Reddish pink Crystal

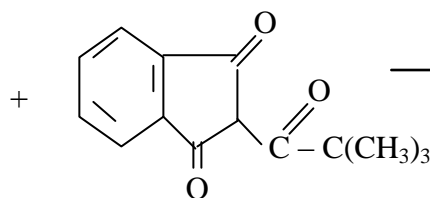
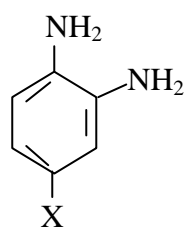


derivative o- phenylene diamine

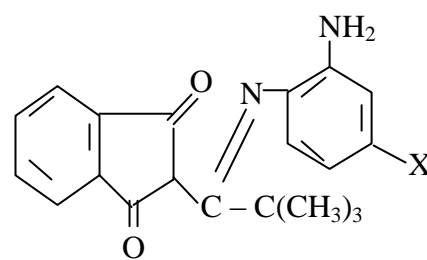
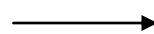
- 1- X = H 2- X = OH ,
 3- X = Br 4- X = NO₂ ,
 5- X = OCH₃ 6- X = COOH



2-pivalloyl-1,3-indanedione



2-pivalloyl-1,3-danedione



β,β' -diketo Schiff base

derivative o- phenylene diamine

(Scheme 2)

2-2: Preparation of Charge-Transfer Complexes Solution .

The CT complexes of β -keto Schiff bases have been investigated with acceptor p-CA(2,3,5,6,-tetra chloro-1,4-benzoquinone),DDQ (2,3-dichloro -5,6-dicyano-1,4-benzoquinone) and TCNE (tetra cyano ethylene) in methylene chloride solution spectrophotometrically at λ_{max} . The measurement of the optical densities of complexes at their λ_{max} were done after 30-60 minutes from the preparation of the complex. The concentrations of all acceptors (1×10^{-4} – 2×10^{-5} mol.dm⁻³) being kept constant in all measurements and the concentration of Schiff bases were variable in every set of solution ,and was much greater than the initial concentration of the acceptor (at least 10 twice) in every solution, this was

done because Bensi- Hildebrand's equation ²⁴ must be held for 1:1 (used Job's method) molecular complex under this condition .(Table 4)

2-3 : Kinetics

The rate of hydrolysis of these Schiff bases were determined spectrophotometrically, all measurements were done with an initial concentration of these compound (1-6) (4×10^{-5} - 4×10^{-4} mol.dm⁻³) at room temperature with Glacial Acetic acid and dilute HCl (30 %), and 50 % Ethanol –Water (w-w) and at their λ_{max} .

2-4 : Electronic Absorption Spectra

The electronic absorption of the new β - β' -diketo Schiff bases (5×10^{-5} - 2×10^{-4} mol.dm⁻³) were measured in different solvents (CH₂Cl₂ , MeOH , DMF , H₂ SO₄ , and CHCl₃).(Table 5)

All measurement of the CT complexes and the hydrolysis and the electronic spectra have been recorded by double-beam Shimadzu (UV-Visible) Spectrophotometer UV-1650 PC, using quartz solution cell (1 cm) path length .

Results and Discussion

1- IR SPECTRA

The IR spectra of the of new(6) β - β - diketo Schiff bases were recorded on Shimadzu Spectrophotometer Fourier Transform (FTIR) as KBr discs .The important bands are given in Table (2) showing the C=O stretching mode for the ketonic group is located at (1620 - 1700 cm^{-1}), while the C=N band appears in the (1588 – 1615 cm^{-1}) region. The spectra show a weak and broad absorption band at (3200 – 3455 cm^{-1}) corresponding to the stretching vibration of the carboxylic OH group (compound 6), the

position and broadening of this band indicate that the OH group is involved in hydrogen bonding (may be bonded or may be over -lapped with stretching mode of NH . The spectra of compound (2) show a strong band at (3410 cm^{-1}) which can be assigned to the stretching vibration of phenolic OH group (give positive test with ferric chloride solution compound (2,3)²⁵).

The NH stretching vibrations appearance band in the IR spectra at (3180 – 3430 cm^{-1}), which assigned to the ketamine tautomer in these compounds^(26,27). Another bands for stretching and bending vibrations of C-H ring and NHetc are estimated. All these confirm that the structure of these compounds are β -diketo Schiff bases and are present in the ketamine - ketimine – enolimine tautomers^(4,5).

Table (2) : The Major IR absorption peaks, measured as KBr discs, and Element Analysis (C.H.N)of the β , β -diketo Schiff bases .

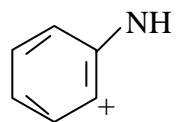
No.S.B	ν OH Cm^{-1}	ν NH Cm^{-1}	ν CO Cm^{-1}	ν C=N Cm^{-1}	δ NO ₂ Cm^{-1}	Element Analysis		
						%cal % C	(found) %H	(found) %N
1		3180 s	1700-1670 m	1600 s		74.02 (75.41)	6.00 (6.60)	8.61 (8.75)
2	3410 m bonded	3350 3320 d 3210 m	1670	1605		71.00 (71.42)	5.11 (5.65)	7.92 (8.33)
3		3240 b	1620 s	1620 s		61.21 (60.30)	5.81 (4.70)	8.00 (7.01)
4	3430 m bonded	3360- 3370 3330 3220	1670	1630 s	1550 1540 1350 sym	66.40 (65.70)	5.90 (5.20)	10.80 (11.51)
5		3430 s 3330 b	1701	1615		71.30 (72.00)	5.60 (6.28)	7.91 (8.01)
6	3455 b	3350 3320	1645	1625		72.10 (72.82)	6.20 (5.49)	6.81 (7.69)

2- Mass Fragmentation

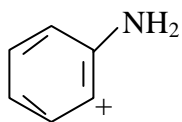
Table (3) show the fragment ions observed in the mass spectrum of compounds (1-6) (the Mass Spectra were recorded on quadruple Mass Spectrometer QMC51 ,Baizers, Fursten tun Liechtenstein with 70 ev energy). Figure (1) represent the mass spectra of molecule (Schiff base 1), which are exhibit an important data used to identify the chemical structure of compounds and to suggested the mechanism of the mass fragmentation pathway of these compounds as showing in scheme (2). The detail mass fragmentation is represents which illustrate clearly the confirmation of the structure of compounds, generally all compounds show a base peaks (m/z at 57,91,92,108 and 171) which take place from the fragmentation of amino ring ions (C(CH₃)₃, C₆H₅N⁺,

C₆H₆N⁺, C₆H₆NO⁺, C₁₀H₅NO₂⁺) respectively by elimination of the β -diketone part, the general fragmentation depends on the kind of substituted on the amino ring (OH , OCH₃ , NO₂ , Br, COOH).The mass spectra show abase peaks (m/z at 17, 314,45, 46,80, 122,136,137) for

Ions (OH , OCH₃ , CO₂ ,COOH , NO₂ , Br, C₆H₄NO₂ , C₇H₆NO₂ , C₆H₅N₂O₂) respectively which take place from the elimination of these ions from the M⁺ ions ,the mechanism of fragment of compounds (1-6) confirms our conclusion concerning the responsibility of the wave length band to the high conjugation owing to charge delocalization in the direction (x-substituent1) to the other part for the molecules^(4,6).



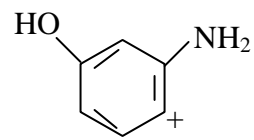
m/z=91
C₆H₅N⁺



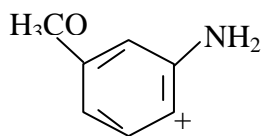
m/z=92
C₆H₆N⁺



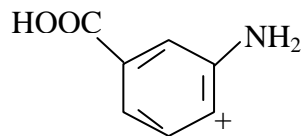
m/z=57
C₄H₉⁺



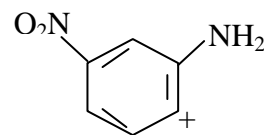
m/z=108
C₆H₆NO⁺



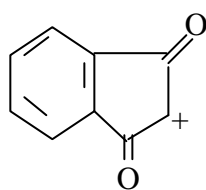
m/z=122
C₇H₈NO⁺



m/z=136
C₇H₆NO₂⁺



m/z=137
C₆H₅N₂O₂



m/z=145
C₉H₅O₂⁺

(Scheme 2)

Table (3): M/Z of The Major Peaks with Their Relative Intensities (I%) which are observed in the Mass spectra of Compounds (1-6).

m/z	compounds						Suggested fragmentation
	1	2	3	4	5	6	
14	42	28	25	62	-	36	[*] NH ₂ , ⁺ CH ₂
17	8	100	-	-	-	58	⁺ OH
18	100	-	-	40	52	23	H ₂ O ⁺
26	22	14	-	-	-	-	⁺ CN
27	15	9	31	11	6	15	H ₂ CN ⁺
28	11	8	-	-	-	63	⁺ CO
30	4	5	8	-	73	5	⁺ NO , ⁺ CH ₂ O
31	-	-	-	-	100	-	⁺ CH ₃ O
42	-	-	-	13	-	-	⁺ CNO
44	-	-	-	-	-	100	⁺ CO ₂
45	-	-	-	-	-	30	⁺ COOH
46	12	14	-	43	8	-	⁺ NO ₂
51	27	16	24	-	16	41	⁺ C ₃ H ₂ N
54	9	-	-	17	8	14	⁺ C ₃ H ₄ N
57	22	28	22	31	15	21	(CH ₃) ₃ C ⁺
67	51	4	18	-	4	3	⁺ C ₄ H ₃ O , ⁺ C ₄ H ₅ N
75	14	14	13	22	25	9	(CH ₃) ₃ COH ₂ ⁺
76	20	4	6	8	12	16	⁺ C ₆ H ₄
77	30	17	11	22	-	8	⁺ C ₆ H ₅
80	-	52	-	-	-	-	Br ⁺
83	14	6	48	-	8	9	⁺ C ₅ H ₉ N
91	30	50	60	52	34	14	⁺ C ₆ H ₅ N
92	29	18	100	26	18	71	⁺ C ₆ H ₆ N : (C ₆ H ₅ NH)
108	-	36	-	-	-	21	⁺ C ₆ H ₆ NO
122	4	-	-	26	41	5	⁺ C ₇ H ₈ NO
136	-	-	-	11	6	80	⁺ C ₇ H ₆ NO ₂
137	-	-	-	100	-	12	⁺ C ₆ H ₅ N ₂ O
154	16	12	14	30	14	22	⁺ C ₉ H ₅ O ₂
151	-	-	-	12	-	-	⁺ C ₆ H ₅ N ₃ O
171	65	14	20	43	54	68	⁺ C ₁₀ H ₅ NO ₂
228	14	24	16	24	15	16	⁺ C ₁₄ H ₅ NO ₂

3 – Charge –Transfer Complexes

Compounds (1-6) interact with p-CA ,DDQ ,and TCNE to form CT complex in CH₂Cl₂ solution the color of these complexes were developed after 30 minutes .Figure (2-4) shows represent the application of Benesi- Hildebrand equation for CT complexes (Eq - 1).Table (4) shows the physical parameters of these compounds (1-6) and of their CT complexes with acceptors. The electronic absorption spectra of the CT complexes of this group display a single CT band with in the λ_{max} (360-418 nm)

range corresponding to the n → π* (intermolecular charge-transfer) with ECT =2.87- 3.62 ev (ECT ,the energy transition of the CT complexes were calculated which revents that the CT complexes formation between the Schiff bases and the acceptors molecules under take place through n→π* bonding (the contribution of π→π* , p-CA ,DDQ ,and TCNE type interaction to complex formation is low or absent) ^(13-15,28).

$$\frac{[A_o].L}{O.D_{CT}} = \frac{1}{K_{CT} \cdot \epsilon_{CT}} \cdot \frac{1}{[D_o]} + \frac{1}{\epsilon_{CT}} \dots\dots\dots(1)$$

[A_o] and [D_o] are the concentrations of the electron acceptor and Schiff bases (electron donor) respectively , L is the path length , O.D_{CT} the optical density of CT complex at λ_{max} . ε_{AD} is the molar extinction coefficient and K_{CT} is the equilibrium constant . The plot of [A_o] / O.D_{CT} Vs 1/ [D_o] gave a straight line

slope = 1 / K_{CT} ε_{CT} and intercept = 1 / ε_{CT}
 K_{CT} = Intercept / Slope = = 1 / ε_{CT} / 1 / K_{CT} ε_{CT}
 The values of ECT is assumption is supported by calculating the entropy of the CT interaction to complexes with acceptors using the relation given by equation(2) ^(24,28-30)
 ECT = I_p - EA - W -----(2)
 And equation (3)

$$ECT = a I_p + b \dots\dots\dots(3)$$

Where EA is the electron affinity of the acceptor (p-CA, DDQ, and TCNE), W is the columbic force between the electron transferred and the positive hole left behind its (4.10 – 5.4 eV), I_p is the ionic potential (9.41 – 10.96 eV) for β -diketo Schiff bases, and the coefficients (a) and (b) are constant for a certain acceptors. Table (4) represent the values of ECT and the ionization potential (I_p) of Schiff bases and the dissociation energies of the excite their CT complexes. From these results I_p and W the electron transfer originates from the same position of each Schiff base s and not affected by the other groups of

molecules to the acceptors^(24,29-31) forming CT complexes of the same geometry for all Schiff bases and obey of Benesi-Hildebrand's equation for 1: 1 CT complexes (the ratio of these complexes also using Job's methods) and the only unoccupied orbital available in p-CA, DDQ, and TCNE is the $n \rightarrow \pi^*$ and the molecules Schiff bases are very rich in electrons, therefore, the value of the physical parameters with the same Schiff bases similarly the type of CT complexes with acceptors are $n \rightarrow \pi^*$ ⁽¹⁰⁻¹⁴⁾.

Table (4) ; The physical parameters of Schiff Bases and of their CT complexes with Acceptors(p-CA, DDQ, and TCNE) in CH₂Cl₂,

No.S.B	CT complex with p-CA				CT complex with DDQ				CT with TCNE			
	λ_{max} CTnm	E_{CT} ev	I_p ev	W ev	λ_{max} CTnm	E_{CT} ev	I_p ev	W ev	λ_{max} CTnm	E_{CT} ev	I_p ev	W ev
1	382	3.24	9.96	5.35	421	3.58	10.45	4.94	418	3.55	10.20	4.45
2	372	3.16	9.87	5.30	415	3.52	10.45	4.94	407	3.04	9.59	4.18
3	384	2.91	9.57	5.14	384	2.87	9.61	4.54	386	2.89	9.41	4.10
4	390	2.92	9.58	5.14	404	3.62	9.83	4.64	386	2.89	9.41	4.10
5	392	3.07	9.76	5.23	398	3.11	10.12	4.78	396	3.11	9.67	4.21
6	360	3.44	10.20	5.46	368	3.37	10.96	5.17	366	3.35	9.96	4.34

4-Electronic Absorption Spectra

The electronic absorption spectra of these compounds (1-6) under investigation exhibited manily four bands (a,b,c,d) λ_{max} value in table (5), the band (a) located at (204-228 nm) are attributed to a local $\pi \rightarrow \pi^*$ excitation of amino rings which affected directly by the substituent, the band(b) located at (250-300 nm) is due to alow energy $\pi \rightarrow \pi^*$ transition within C=O, the band (c) located at (311- 356 nm) is due to the $\pi \rightarrow \pi^*$ within C=N, and the band(d) at (370-415nm) can be assigned to an intramolecular charge transfer with in the whole molecules (CT), which are red shifted upon increasing conjugation in the molecules which indicate formation of β -diketo Schiff bases⁽⁴⁾. The electronic absorption of the new β , β -keto Schiff bases were measured in organic solvent of varying polarity CH₂Cl₂, MeOH, DMF

,CHCl₃, and concentrated H₂SO₄, the long UV band of almost compounds are bath chromic shift because the excited state must be more polar than the ground state which is stabilized by polar solvent (in the conc. sulfuric acid which draw all the nitrogen electron ion pair should occurs. The four band in the electronic spectra of compounds(1-6) in different solvent is a probably assigned to the $\pi \rightarrow \pi^*$ transition which is originated from amino rings. Compounds in polar solvent gives a highly colored complexes with ferric chloride solution (positive test) which means that the enol tautomers present in an appreciable ratio. The electronic spectra of these compounds show absorption bands near 400nm represent the ketamime tautomer for these Schiff bases in high polar and hydroxylic solvents^(4,32-34).

Table (5): Electronic absorption spectra of β , β -diketo Schiff bases (5×10^{-5} - 5×10^{-4} mol.dm⁻³) in different solvents(in nm).

No.S.B	solvent	PhN	C=O	C=N	CT
1	CH ₂ Cl ₂	214	282	338	346
	MeOH	212	290	338	350
	DMF	250	314	337	370
	H ₂ SO ₄	228	296	342	368
	CHCl ₃	252	302	338	352
2	CH ₂ Cl ₂	211	292	341	350
	MeOH	218	298	340	256
	DMF	236	308	341	374
	H ₂ SO ₄	214	-	352	361
	CHCl ₃	222	305	340	358
3	CH ₂ Cl ₂	209		335	354
	MeOH	212	271	339	353
	DMF	-	270	344	376
	H ₂ SO ₄	217	270	332	360
	CHCl ₃	237	282 305	340	356
4	CH ₂ Cl ₂	214	278	326	396
	MeOH	212	274	320	400
	DMF	-	286	315	385
	H ₂ SO ₄	224	292	314	382
	CHCl ₃	-	277,288	317	382
5	CH ₂ Cl ₂	204	288	348	-
	MeOH	210	284	344	-
	DMF	208	278	346	365
	H ₂ SO ₄	212	-	-	352
	CHCl ₃	212	288	346	250
6	CH ₂ Cl ₂	208	276	344	362
	MeOH	209	268	305	370
	DMF	226	282	316	367
	H ₂ SO ₄	214	-	322	372

5 – Kinetics of Hydrolysis

For every decay curve the variation of % Transmitted light with time (Fig 5-7) was replotted as optical density ($-\ln O.D$) vs. time), a very good straight line was obtained in every case which indicates that the hydrolysis of the Schiff base in 50 % aqueous solution of ethanol or its mono-acid ion (gl.acetic acid , dilute hydrochloric acid) is strictly first order kinetics , the slope of the line represents the observed pseudo first-order constant (Kobs) ,

The hydrolysis in each case was followed until 90% completion . Eq(1-5) represent the differential equation of the first order reaction⁽³⁵⁾

$$\ln \frac{a}{a-x} = k t \text{ -----(1-5)}$$

From Lambert- Beert law $O.D = \epsilon.C.L$ ----- (2-5)

O.D ; optical density

$$\ln \frac{O D_0}{O D_t} = k t \text{ -----(3-5)}$$

($O.D_0$, $O D_t$, is the optical density at zero time and (t) time respectively.)

Rearrangement of equation $-\ln (O.D)t = k t - \ln (O.D)o$ -----(4-5)

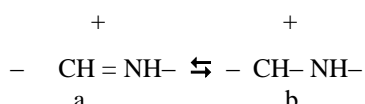
The plot of $-\ln (O.D)t$ vs. (t) should give a straight line with a slope equal to (k) and intercept equal to $-\ln (O.D)o$.

The stability of the Schiff bases mono- acid in terms of ($t^{1/2}$) is calculated from equation(5-5)⁽³⁵⁾

$$t^{1/2} = \ln 2 / k = 0.693 / k \text{ ----- (5-5)}$$

The stability of anilium ion of compounds (2,5,6) in 50 % ethanol and gl.acetic acid (Table 6,7) is higher than compound (3,4) owing to the presences of Br , NO 2 (drawing groups) .The unusual stability of the anilium ion which was explained in term of delocalization of the change through resonating structure involving the phenylene ring of the molecules the decrease or the increase in the optical density at λ_{max} with time were measured . The higher stability of the anilium ions in gl.acetic acid with that in dilute acid (30 %) solution due to the avery small concentration of water present in the former medium .Since Schiff bases are readily hydrolysis in aqueous acid solution (Fig 5-7), (in gl.acetic acid and HCl where a proton is added to the azomethine).These Schiff base (as a salt) are readily dissociation in water releasing the free Schiff bases .Compound (2,5,6) have been hydrolyze slower than compound (3,4) and its substituted derivatives (other) due to the hydrogen bonding complex in

compound(1,3,4),then H-bonding complexes stabilized these compound and make their hydrolysis slower formation H- bonding in neutral aqueous solutions water molecules play a draw of the acid and nucleophile to form the carbonium ion by the attack of the azomethine group , the carbonium ion character of the conjugate acid stabilized by delocalization of the charge, (structure a,b) which in turns increase with increasing planarity of the Schiff bases molecules. The observed first order rate constants are summarized in table (6-8) . The subsistent in the amine ring molecules reduce the rate of hydrolysis approximately by the same amount .



The carbonium ion is hydrolytically cleaved through the formation of carbinol amine intermediate(-CHOH-NH-) in neutral solutions(which may be accounted for in terms of either rate-determining water attack on the free substrate under slightly acidic conductions in which the Schiff bases is nearly rate determining attack of water on the protonated substrate⁽³⁶⁾. In the acid medium the rate of the hydrolysis of the Schiff base follows generally the rate equation.

$$\text{Rate} = - d [\text{BH}^+] / d t = k_1[\text{BH}^+] [\text{H}^+] + K_2[\text{BH}^+]$$

Where $[\text{BH}^+]$ is the concentration of the protonated Schiff base molecule, k_1 and k_2 are constants. In acid medium yielding complete hydrolysis to the corresponding β -diketon and the primary amine as show in equation follows^(17,36) :



Table (6) ; Stability of Schiff Bases (1-6) in 50% Ethanol .

Compds .No. *	λ_{max} nm	$K_{\text{obs}} \times 10^{-2} / \text{min}^{-1}$	Stability in terms of $t_{1/2} / \text{min}$	No of exps
1	342	2.90	23.89	3
2	348	2.3	29.24	3
3	352	3.12	22.21	3
4	398	3.17	21.86	3
5	364	2.50	27.72	2
6	362	2.65	26.15	3

*- All measurement were done 30 ± 2 °C and with an intial concentration of Schiff Bases ($4 \times 10^{-5} - 4 \times 10^{-4}$ mol .dm⁻³)

Table (7) ; Stability of Schiff Bases (1-6) in Glacial Acetic Acid.

Compds .No. *	λ_{max} nm	$K_{\text{obs}} \times 10^{-2} / \text{min}^{-1}$	Stability in terms of $t_{1/2} / \text{min}$	No of exps
1	382	8.91	7.77	2
2	387	2.22	31.12	3
3	381	9.80	7.07	3
4	442	14.11	4.9	3
5	374	8.06	8.59	3
6	398	8.70	7.96	3

*- All measurement were done 30 ± 2 °C and with an intial concentration of Schiff Bases ($4 \times 10^{-5} - 4 \times 10^{-4}$ mol .dm⁻³)

Table (8) ; Stability of Schiff Bases (1-6) in 30% Hydrochloric Acid .

Compds .No.	λ_{max} nm	$K_{\text{obs}} \times 10^{-2} / \text{min}^{-1}$	Stability in terms of $t_{1/2} / \text{min}$	No of exps
1	348	9.55	7.25	3
2	351	4.68	14.8	3
3	356	10.19	6.8	3
4	386	21.03	3.29	3
5	344	7.40	9.36	2
6	367	8.00	8.66	3

*- All measurement were done 30 ± 2 °C and with an intial concentration of Schiff Bases ($4 \times 10^{-5} - 1 \times 10^{-4}$ mol .dm⁻³)

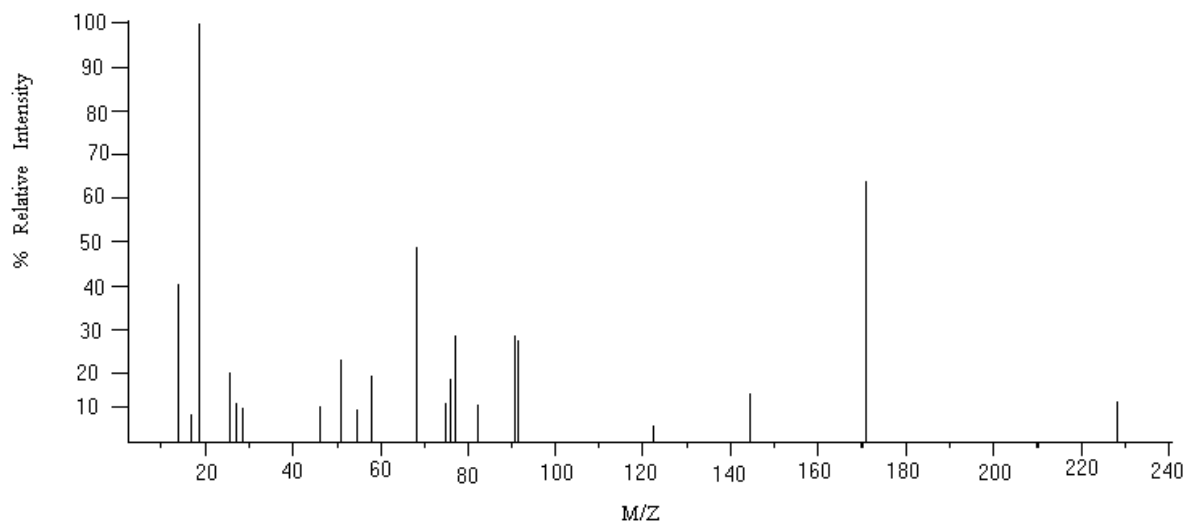
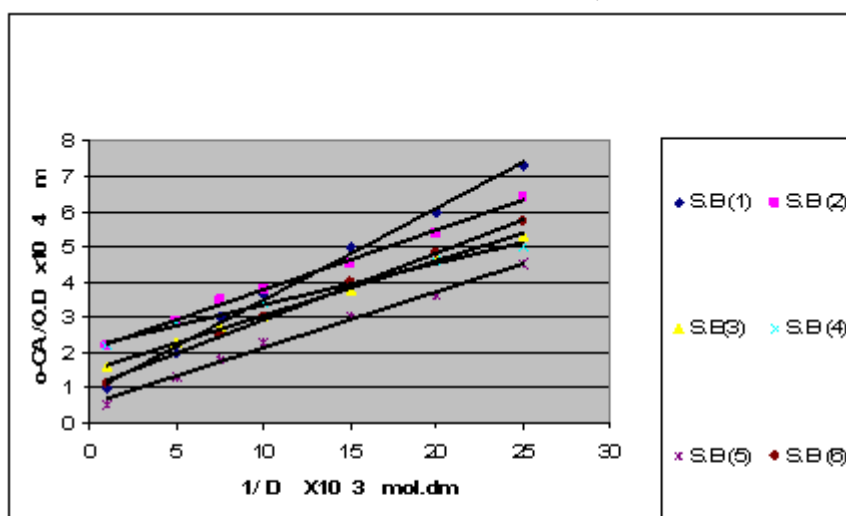


Figure (1) : Mass spectrum of Molecule 1 (Schiff base 1)

Fig(2):Application of Benesi-Hildbrands Equation for the CT complexes of Schiff bases (1-6) with p-CA in CH₂Cl₂.



Fig(3):Application of Benesi-Hildbrands Equation for the CT complexes of Schiff bases (1-6)with DDQ in CH_2Cl_2 .

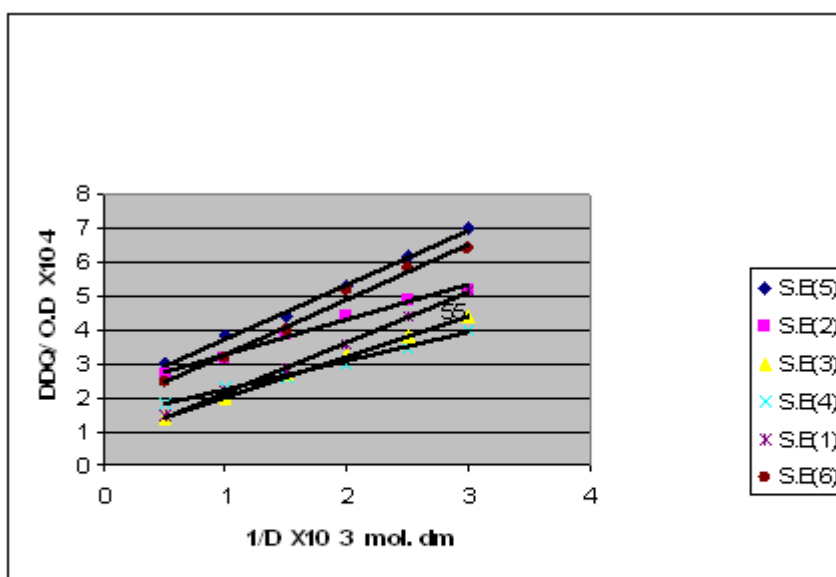
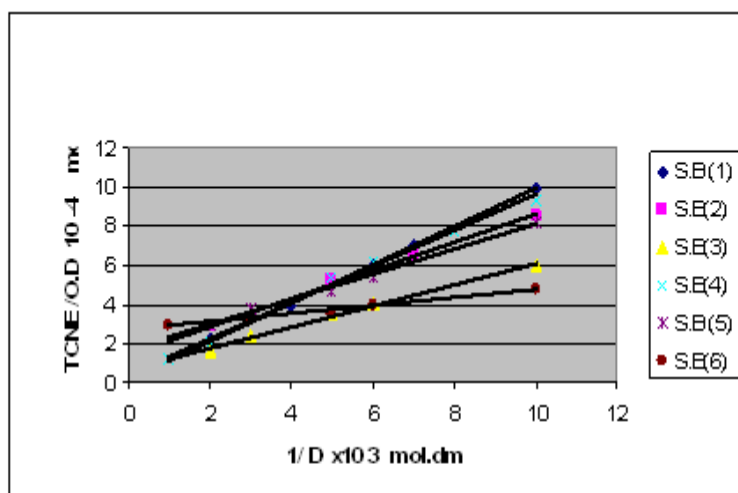
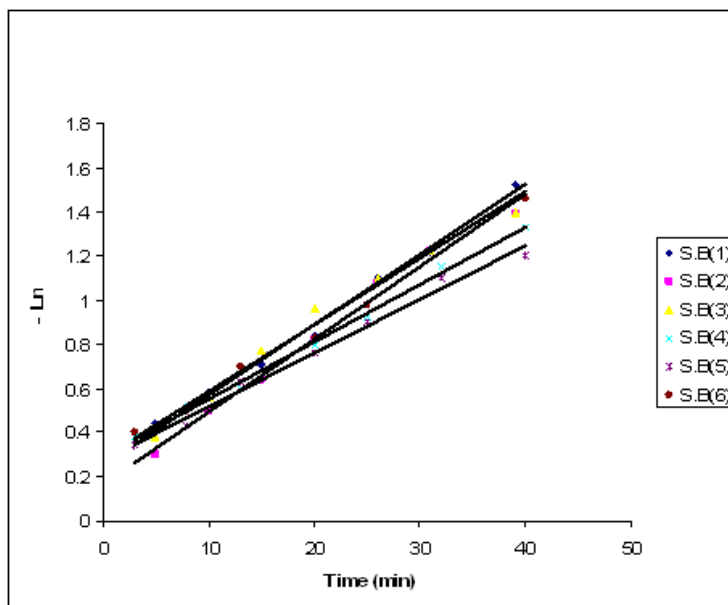


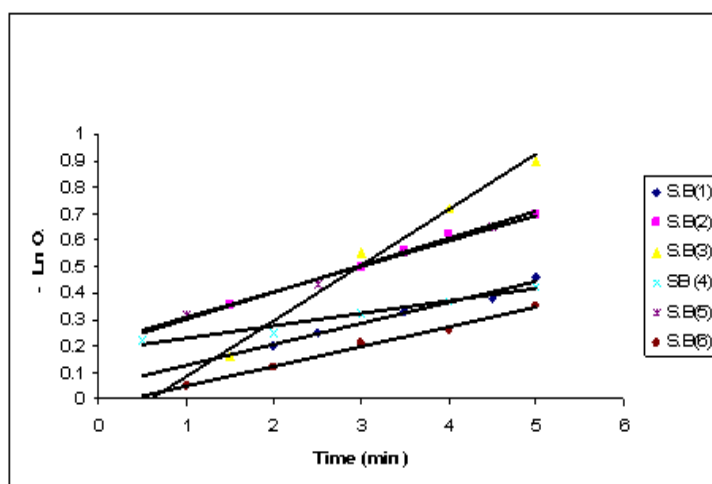
Fig (4):Application of Benesi-Hildbrands Equation for the CT complexes of Schiff bases (1-6)with TCNE in CH_2Cl_2



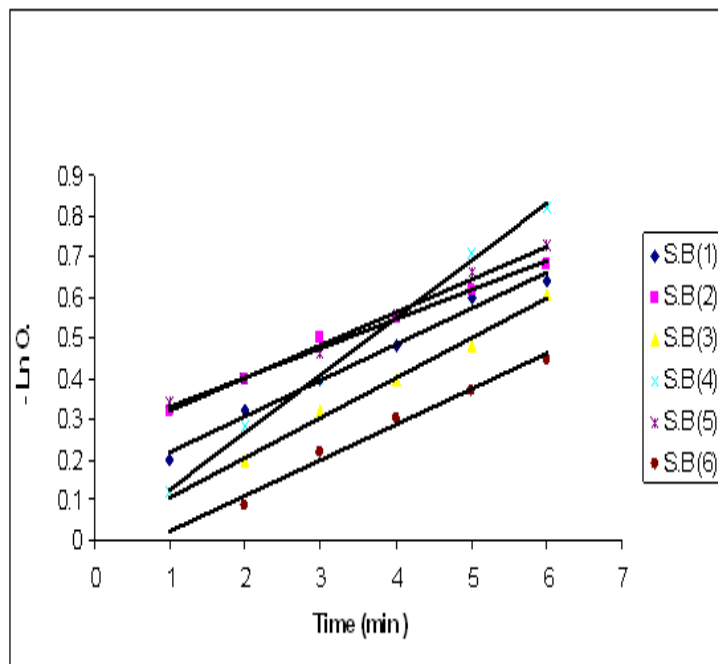
Fig(5): A typical first order kinetic plot for the hydrolysis Schiff bases (1-6) in 50% C₂H₅OH



Fig(6): A typical first order kinetic plot for the hydrolysis Schiff bases (1-6) in 30% HCl



Fig(7): A typical first order kinetic plot for the hydrolysis Schiff bases (1-6) in gla.CH₃COOH.



Conclusion

In conclusion it can be summarized as follows :_

- 1-The molecular structures of these new Schiff bases (1-6) characterized and identified.
- 2-The electronic spectra in dichloro methane solution were used to study the intermolecular CT complexes between our Schiff bases as charge donors and p-CA, DDQ and TCNE as charge acceptors, form these spectra some physical parameters are calculated . The solution of

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all complexes are obeyed to Benesi-Hildbrands equation which means that the ratio 1:1,all complexes are of $n \rightarrow \pi^*$ type in every case.

- 3- The effect of polar , non-polar solvent on the electronic transition have measured and discussed.
- 4-The average value of k_{obs} for each hydrolysis in different mediu depending upon the disappearance of these compound (1-6).

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دراسة طيفيه وحركية لبعض قواعد شف الجديدة من بيتا- ثنائي كيتون المشتقه من ٢

- بايفولايل - ٣،١ أندان دايون

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الملخص

يتضمن البحث تحضير قواعد شف الجديدة من نوع بيتا- ثنائي كيتون الناتجة من تكثيف ٢ -بايفولايل - ٣،١ اندين دايون مع ستة معوضات مشنقة من اورثو- فنبيلين ثنائي أمين وتشخيص وتعين التراكيب الجزئية لهذه القواعد بواسطة تقنية الأشعة تحت الحمراء و طيف تجزؤ الكتلة وتحليل العناصر. ويتضمن البحث دراسة معقدات انتقال الشحنة لهذه القواعد مع ثلاث مستقبلات الكترونية وتعين بعض المتغيرات الفيزيائية لهذه القواعد ومعقدات انتقال الشحنة. بالإضافة إلى دراسة تأثير المذيبات المختلفة في القطبية على هذه القواعد ودراسة حركية التحلل لهذه القواعد في أوساط مائية وحامضية.