Estimation of the physical constants of the electron acceptor 1,4-naphthoquinone from its charge-transfer complexes with various Schiff bases n-type donors

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الخلاصة

تمت طيفياً دراسة معقدات انتقال-شحنة جديدة لإحدى عشرة قاعدة من قواعد شيف ومشتقاتها الأليفاتية كمركبات واهبة للشحنة نوع n مع مستقبل الشحنة أو الإلكترون 1، 4-نفثوكوينون بالمنطقة فوق البنفسجية – المرئية (الإلكترونية) بمذيب الكلوروفورم. حسبت و نوقشت في هذه الدراسة الثوابت الفيزيائية والقيم المفيدة للمستقبل (Ea,C2,C1,b,a) و كانت كالأتي 1.39,1.92,7.067,-4.157,0.8385 الكترون فولت على التوالي. حيث a = ثابت ميل وانحدار المستقيم المرسوم والمستخرج من معادلة الدرجة الأولى hv =aIp + b و b = ثابت ونقطة تقاطع الخط المستقيم المرسوم بموجب معادلة الدرجة الأولى hv =aIp + b. كذلك C1 و C2 ثوابت فيزيائية محسوبة للمسقبل بموجب المعادلة (3).، Ea = الالفة الالكترونية للمستقبل و ا لمحسوبة من معادلة رقم (1). وحسبت و نوقشت أيضا المعاملات الفيزيائية لمعقدات انتقال- الشحنة من معادلةالدرجة الأولى ، معادلة بنسي – هيلد براند حيث ثابت الميل والانحدار = εK/1، ثابت الموازنة=K و ثابت الامتصاص المولاري منy=ε/1 ومعدل طاقات تفكك حالات الإثارة للمعقدات والمساوية لـ (4.70) الكترون فولت المحسوبة بموجب المعادلة(5).

ABSTRACT

The new charge-transfer complexes (CT) of eleven Schiff bases molecules as n-electron donors with the acceptor 1,4-naphthoquinone were studied spectrophotometrically in chloroform solution. The physical constants (a,b,C1,C2,Ea) of 1,4-naphthoquinone were calculated and they are 0.8385, -4.157, 7.067, 1.92, 1.39 electron volt respectively.where a= slop of straight line of first order equation , hv= aIp + b, b=y = interept of first order equation ,(b = hv – aIp), C1 and C2 are physical constants of acceptor (eq.3.) ,Ea = electron

affinity of 1,4 –naphthoquinone ,which is calculated from equation (1). The physical parameters of the (CT) complexes, of Benesi- Hildebrands equation; (1/(έ K))= slop of equation=a, b=1/έ =intercept y of the straight line of benesi-Hildebrands equation (of first order),where the molar extinction coefficient= ε and K= the equilibrium constant of the formation of bond n-pi (CT) complexes , the average dissociation energies of the excited state W=4.70 eV were also calculated and discussed.

Key words:

Charge-transfer complexes (CT), 1,4-Naphthoquinone,Physical chemistry of donor, Acceptor,Aliphatic aldehyde,Valence bond theory,Schrodinger equation and quantizatin ,Donor of aliphatic Schiff bases(azomethines) p-N,N-dimethylaminocinnamaylidenes, Aromatic primary amine ,Electromagnetic light photon, 1,4-Quinones and carbonyl conjugation chemistry, Physical calculation, Benesi-Hildebrand's equation ,Aliphatic substituents and their effects, Education and science studies. HOMO ⟶ LUMO transition.

INTRODUCTION

Previously benzoquinones such as 1,4-benzoquinones, 9,10-anthraquinones [1], 2 , 3 - dichloro-5 , 6- dicyano-1 , 4-benzoquinones [2-4], 2 , 3 , 5 , 6 - tetrachloro-1,4-benzoquinones-chloranil CA[3-8] and 3,5 ditert-butyl-1,2- benzoquinones[1] had been used as electron acceptors with various Schiff bases as n-electron donors forming n ⟶ Л charge transfer (CT) in the (CT) process. Other electron acceptors such as iodine [4,9-11,12], pentafluorbezaldehyde PFB[6-8], tetracyanoethylene[3] and tetracyanoquinodimethane form also (CT) complexes with various kinds of Schiff base compounds.

In the present work, the (CT) complexes between 1,4-naphthoquinone [1,4-Nq] and some Schiff bases(azomethines) derived from aliphatic aldehyde, p-N,N-dimethylaminocinnamaldehyde, and different anilines were investigated spectrophotometrically in $CHCl_3$ solutions.

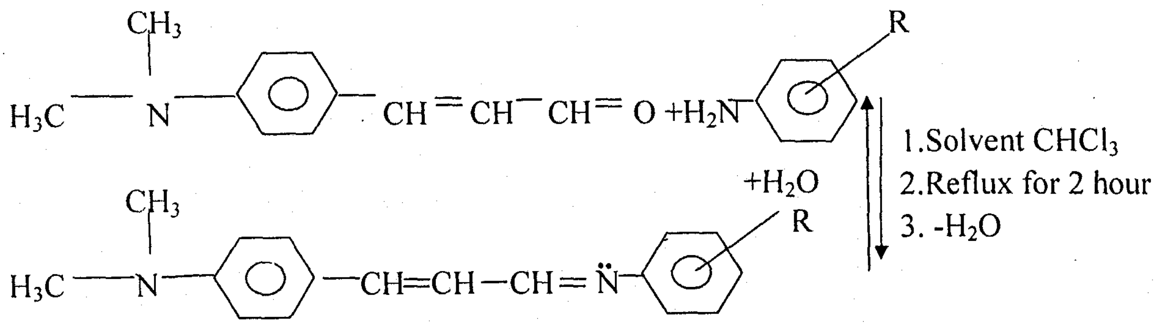
The physical constants of [1,4-Nq] and some physical parameters of the (CT) complexes have been calculated and discussed.

EXPERIMENTAL

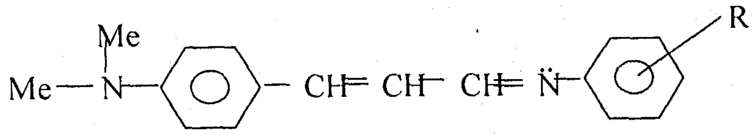
Schiff bases, compounds 1-11 (Scheme 1) were prepared and purified as described in the literature [6-8]. 1,4- naphthoquinone (97% purity) was of "Aldrich", and chloroform (Spectrosil) was of "Fluka". Beckmann spectrophotometer, Acta-M.VII, thermostat 298K , Schimatzu uv-vis. Recoding Spectrophotometer uv-160 were used to record the electronic spectra using 1.0 cm quartz cell,uncorrected balance,elemental analysis (C,H,N,O,)were carried out by oil research center/ Al-Habibya-Baghadad.

The solution of (CT) complexes in $CHCl_3$ were prepared by mixing of fixed concentrations of [1,4-Nq[and variable concentration of Schiff bases where [Schiff base]>>[1,4-Nq], Benesi-Hildebrand's equation of absorption is applicable to 1:1 (acceptor- donors) molecular n-pi (CT) complexes only under this condition[2,5-8,13,14]. In every solution of the set the concentration of the aliphatic Schiff base(azomethine) was the same in both the reference cell and the sample cell .

a. Reaction equation of preparation and formation of Schiff bases: The synthesis of cinnamaylidenes Schiff bases and its derivatives from the starting materials, the aldehyde and the anilines (primary aromatic amines) were completed as in the following:



..The prepared and formed Schiff bases and their derivatives are as in scheme 1:



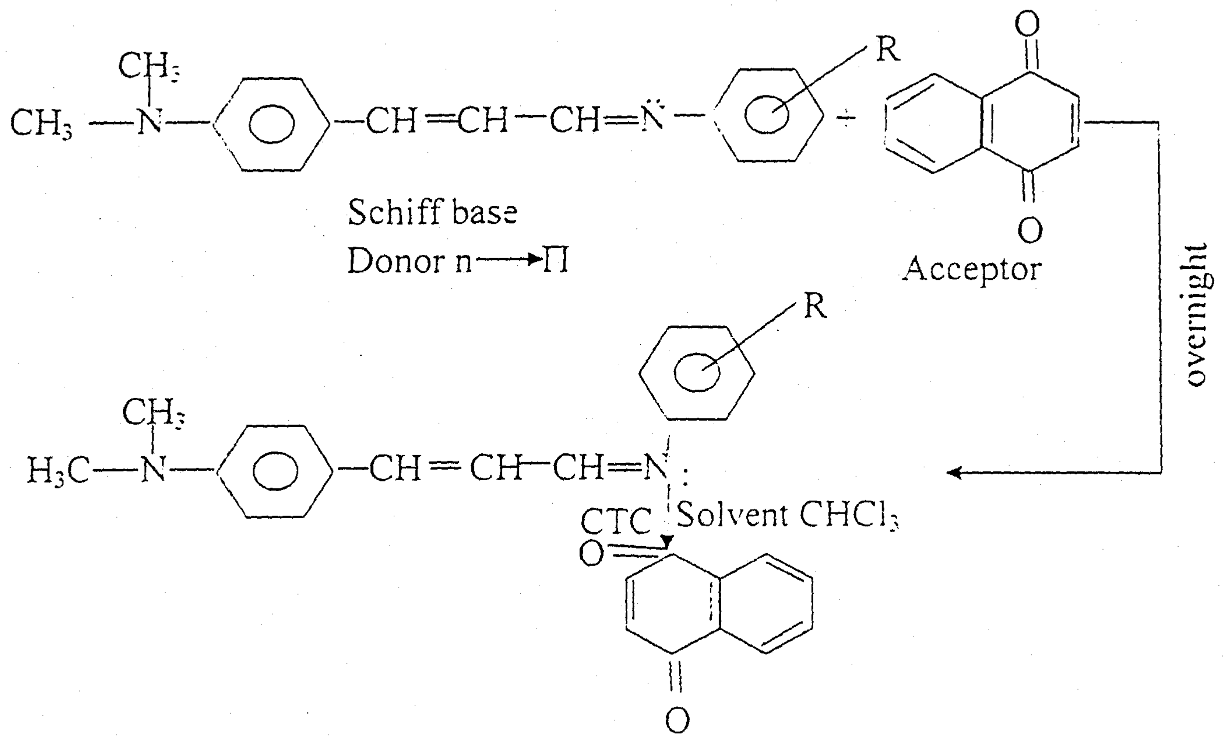
where R represent the substitutional decreasers and increasers of charge and they are;

1. R=-Cl (p),
2. R=-Br (p),
3. R=-NO2 (p),
4. R=-COOH (p),
5. R=-H,
6. R=-CH3 (p),
7. R=-CH3 (m),
8. R=-OCH3 (p),
9. R=-OCH3 (m),
10. R=N(CH3)2 (p),
11. R=-OH (p).

Scheme (1)Aliphatic Schiff bases(azomethines) formation by reaction pathways

Table (1) illustrates the expected, molecular formula and elemental analysis to the (1-11) above aliphatic Schiff bases (azomethines)structures.

b. Reaction equation of (CT) complexes formation: Synthesis of charge-transfer complexes of n-piл bond was yielded from its starting materials Schiff bases as n-electron donors and the 1,4-naphthoquinone as new acceptor; The yielded and suggested product CTC[between 1,4- nq acceptor and n-donor Schiff base]was prepared as in the following:



Scheme (2) CTC
The unique product; charge transfer
complex (p-N,N-dimethylaminocinnamaylideneanilines-1,4-naphthoquinone.)

RESULTS AND DISCUSSION

3-1 Estimation of the physical constants of [1,4-Nq]

Table (2) represents the longer wave length absorption bands in the electronic spectra of [1,4-Nq] and molecules 1-11, the ionization potentials (Ip) of (1-11) structures and their transition energies (hv) with the acceptor [1,4-Nq], and their transition energies with the acceptor PFB in $CHCl_3$.
From the data of table (2) and the electron affinity of PFB (E_a=1.37 ev)(6-8), the physical constants a,b,C_1,C_2 and Ea [1,4-Nq] of the acceptor [1,4-Nq] have been calculated using equations (1-3)([6-8,12,13,14]).

$$Ea[1,4\text{ - NQ}] = \text{Ea(PFB) - hv(PFB) + hv}[1,4\text{ - NQ}] \quad (1)$$

where E_a = electron affinity,and hv= CT energy

$$hv[1,4\text{ - NQ}] = \text{a Ip + b} \quad (2)$$

$$hv[1,4\text{ - NQ}] = \text{Ip - } C_1 + \frac{C_2}{\text{Ip - }C_1} \quad (3)$$

For the CT complexes of [1,4-Nq] with the donor of Schiff base(azomethine) molecules (1-11) in $CHCl_3$, Figures (1-11), the values were summarized in table (3).
The values of table (3) agree very well with those of the benzoquinone acceptors(2,5-8,11).

3-2 Estimation of the physical parameters of (CT) complexes:

Table number four(4) shows the values of the molar extinction coefficient of (CT) complexes ε, the equilibrium constant of formation of n-pi (CT) complexes K, and the dissociation energies of the (CT) complexes of the excited states W in CHCl3.(spec.CHCl3 is a good solvent suitable to the CT process and less spectral complication than alcohol as expected.).
. The values of ε and K were calculated using Benesi-Hildebrand's equation(4) (5-8,10,11).

$$\frac{1.[1,4-NQ]}{OD_{CT}} = \frac{1}{\varepsilon.K}\frac{1}{[SB]} + \frac{1}{\varepsilon} \quad (4)$$

Where [1,4-Nq] and [SB] are the initial concentrations of the acceptor 1,4-naphthoquinone and Schiff base respectively (scheme 1); ODCT is the optical density or absorbance of (CT) complexes at electromagnetic light radiation of photon wave λmax , (table (4));

l. is the path length of the light photon absorption cell (=1.0 cm(10 mm.)). The plots of [1,4-Nq].1/ODCT vs. the values of 1/[SB] gave according to the equation (4) a very good straight lines (figures (1-11) show a typical examples) of which the intercept y is equal to $1/\varepsilon=b$ and the slop is equal to($1/(\varepsilon.K))=a$; then from both the intercept and the slop, ε and K can be evaluated, table(4) illustrated the results.

The data of tables (2) and (4) show clearly that the presence of strong electron-donating groups(15) such as $-OCH3$ (p), $-N(CH3)2$ (p) and -OH (p) in molecules 8, 10 and 11 (scheme 1), enhance the ($n \longrightarrow \pi$) (CT) complexes formation; K=778, 730, 832 mol-1dm3, respectively(tables (2,4)) . The presence of electron-donating groups(the increasers) in the structures of such compound increase the electronic density of their azomethine groups, which makes these strong n-electron donors, $>C=\ddot{N}\rightarrow$ in comparison with the other molecules, unlike those, deficiency at nitrogen atom resulted from electrons-withdrawing groups or the decreasers of the process of which have relatively low (CT) complex formation because of less formed electrons transition, [-NO2, K=61, cpd 3], [-COOH, K=97 cpd 4] and this deactivation of the azomethine nitrogen pair of electron in less reactive Schiff bases resulting the destabilized CTC, and this is in a good coincide with reactivity of groups in physical organic chemistry..etc(3,7,13,15).

The CT process is governed by n-electron donation from the azomethine group of aliphatic Schiff base(azomethine) molecule to the empty π orbital of the carbonyl groups of [1,4-Nq] acceptor forming and yielding $n \longrightarrow \pi$ CT complex (HOMO to($\longrightarrow$) LUMO electronic transition and since the more conjugation is added, the longer wave length is obtained, table (2), figures (1-12).

The values of Δ or W evaluated from the data of tables(2,3) using equation(5-8,13,14). (5)

$$\Delta or W = Ip - Ea[1,4-NQ] - hv[1,4-NQ] \quad (5)$$

where W=dissociation energies of CTC excited states = 4.70 eV

Ip = Ionization potential of donor or Schiff base(azomethine) eV

Ea[1,4-Nq.] = Electron affinity of acceptor---------------------- eV

hv = CTC energy --- eV

1,4-Nq =1,4 –Naphthoquinone

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Table (1) Molecular formula and elemental analysis of p-N,N- dimethylaminocinnamaylidenes or the prepared Schiff bases as n-type charge (electron) donors

R The substitu-tion	Molecular formula of Schiff bases	Elemental analysis					
		Calculated			Founded		
		%C	%H	%N	%C	%H	%N
1-Cl (p)	$C_{17}H_{17}N_2Cl$	71.70	5.97	9.84	71.36	5.90	9.53
2-Br (p)	$C_{17}H_{17}N_2Br$	62.00	5.16	8.51	62.01	5.14	8.60
3-NO₂ (p)	$C_{17}H_{17}N_3O_2$	69.15	5.76	14.23	69.00	5.60	14.15
4-COOH (p)	$C_{18}H_{18}N_2O_2$	73.46	6.12	9.52	73.13	6.00	9.50
5-H (p)	$C_{17}H_{18}N_2$	81.60	7.20	11.20	81.62	7.10	11.40
6-CH_3 (p)	$C_{18}H_{20}N_2$	81.81	7.57	10.60	81.60	7.50	10.65
7-CH_3 (m)	$C_{18}H_{20}N_2$	81.81	7.57	10.60	81.70	7.50	10.50
8-OCH_3 (p)	$C_{18}H_{20}N_2O$	77.14	7.14	10.00	77.00	7.14	10.01
9-OCH_3 (m)	$C_{18}H_{20}N_2O$	77.14	7.14	10.00	77.03	7.17	10.01
10-$N(CH_3)_2$ (p)	$C_{19}H_{23}N_3$	77.81	7.84	14.33	77.71	7.82	14.10
11=-OH (p)	$C_{17}H_{18}N_2O$	76.69	6.76	10.52	76.45	6.76	10.50

Table (2), The longer wavelength absorption band in the electronic spectra of 1,4-Nq,and the formed Schiff bases molecules 1-11, and their ionization (Ip) and CT transition energies hv and their CT transition energies with the PFB in $CHCl_3$

Compound No.	Compound Longer λ/nm	CT with 1,4-Nq		CT with PFB(*)		
		λ/nm	hv/eV	λ/nm	hv/eV	Ip/eV
1,4-Nq	333	-	-	-	-	-
1	394	536	2.30	528	2.35	8.42
2	396	540	2.29	530	2.34	8.41
3	388	544	2.28	570	2.17	8.22
4	398	447	2.78	544	2.28	8.34
5	390	525	2.36	510	2.43	8.51
6	386	557	2.42	506	2.45	8.53
7	385	526	2.36	514	2.44	8.41
8	392	528	2.35	508	2.44	8.52
9	386	516	2.40	516	2.40	8.47
10	382	544	2.28	236	2.31	8.37
11	388	513	2.42	510	2.43	8.51

- Data taken from reference (8)

Table (3), The values of the physical constants of the acceptor 1,4-Nq from its CT complexes with molecules of aliphatic Schiff bases(azomethines) 1-11 in $CHCl_3$

The CT with compound	a/eV	b/eV	C_1/eV	C_2/eV	E_a/eV	Δ or W of CTC
1-11	0.8385	-4.157	7.067	1.9 2	1.39	4.70

Table (4), The molar extinction ε of the CT complexes, the equilibrium constant K of the formations, and the dissociation energies of the CT complexes at excited states W or (Δ) in $CHCl_3$

Compound No.	CT with [1,4- NQ]		
	ε/m^2mol^{-1}	$K/mol^{-1}dm^3$	W or (Δ) eV
1	16600	330	4.78
2	1650	313	4.78
3	20020	61	4.60
4	12400	97	4.22
5	8002	631	4.81
6	2600	482	4.77
7	2200	312	4.71
8	6669	728	4.83
9	2600	321	4.73
10	1670	730	4.75
11	785	832	4.75
Average	-	-	4.70

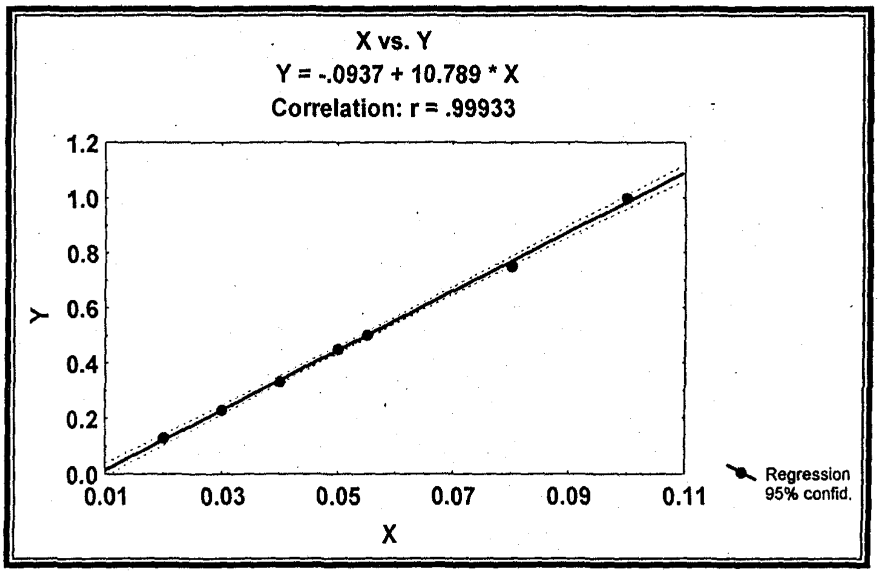


Fig.1 –Cl(p)

$$\lambda_{\max} = 536nm$$

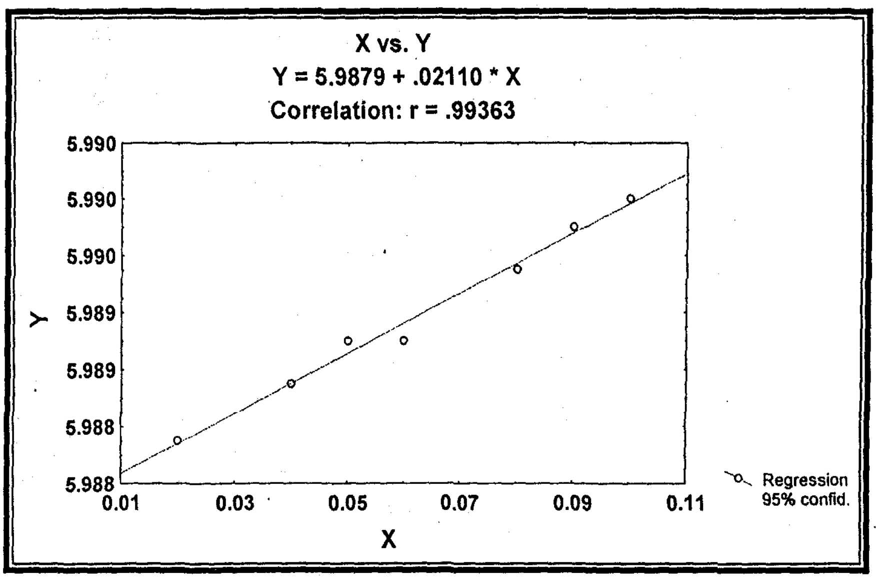


Fig.2 –Br(p)

$$\lambda_{\max} = 540nm$$

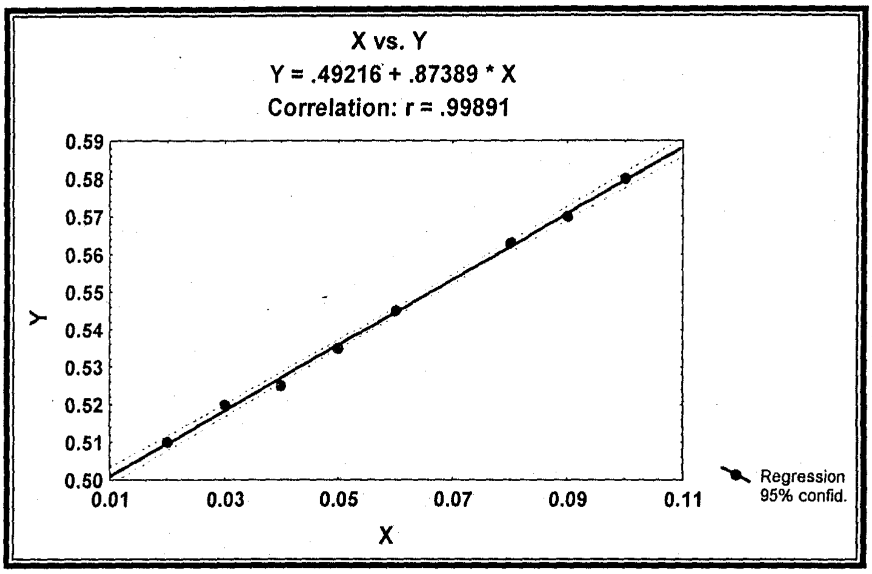


Fig.3 –NO_2(p)

$$\lambda_{\max} = 544nm$$

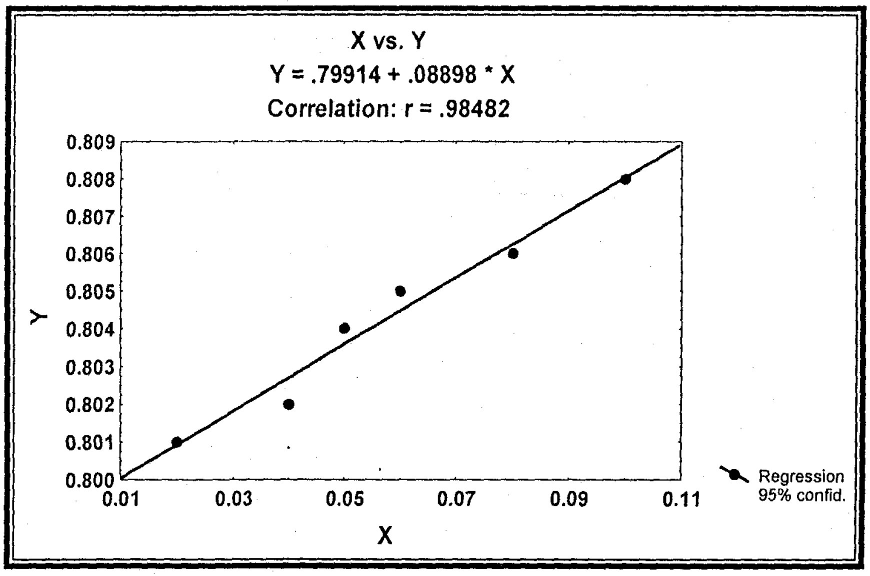


Fig.4 –COOH(p)

$$\lambda_{\max} = 547nm$$

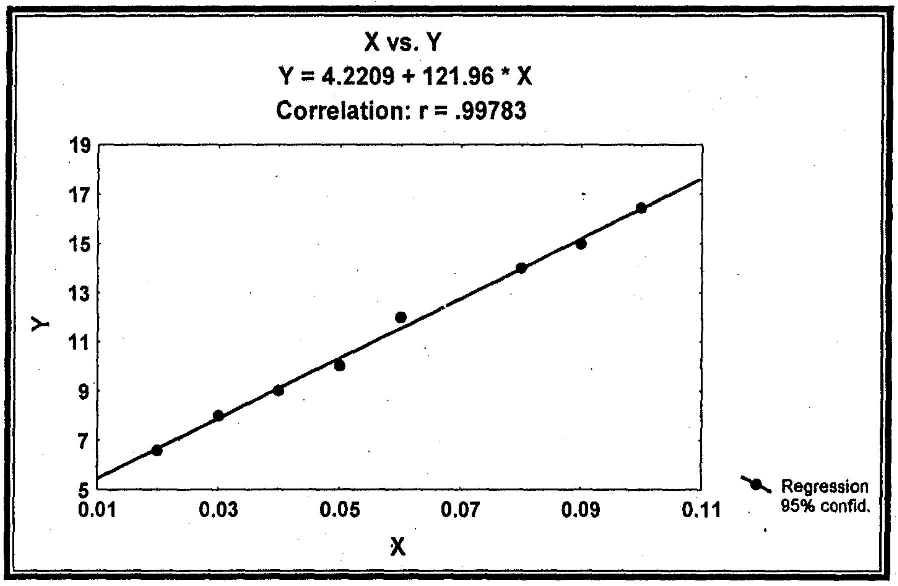


Fig.9 –OCH$_3$(m)

$$\lambda_{\max} = 516nm$$

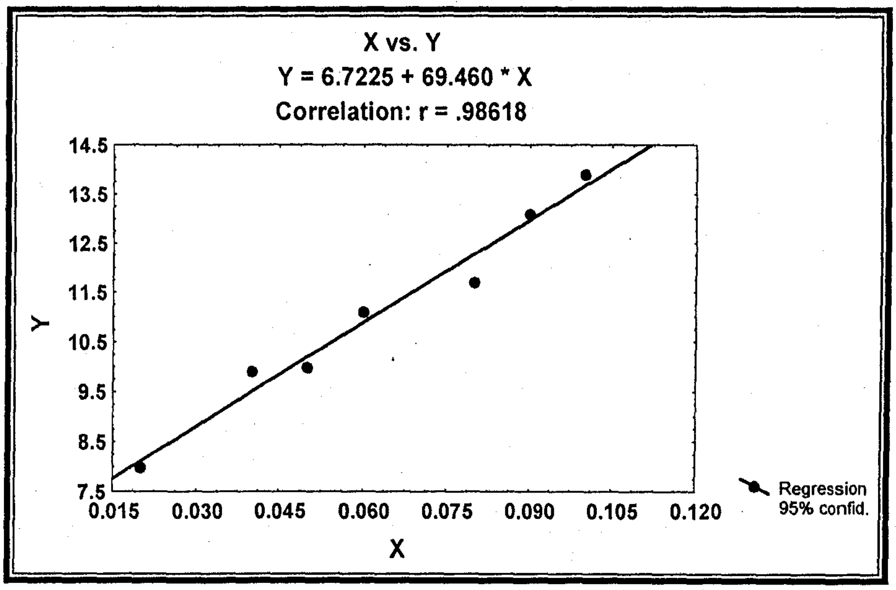


Fig.10 –N(CH$_3$)$_2$(p)

$$\lambda_{\max} = 544nm$$

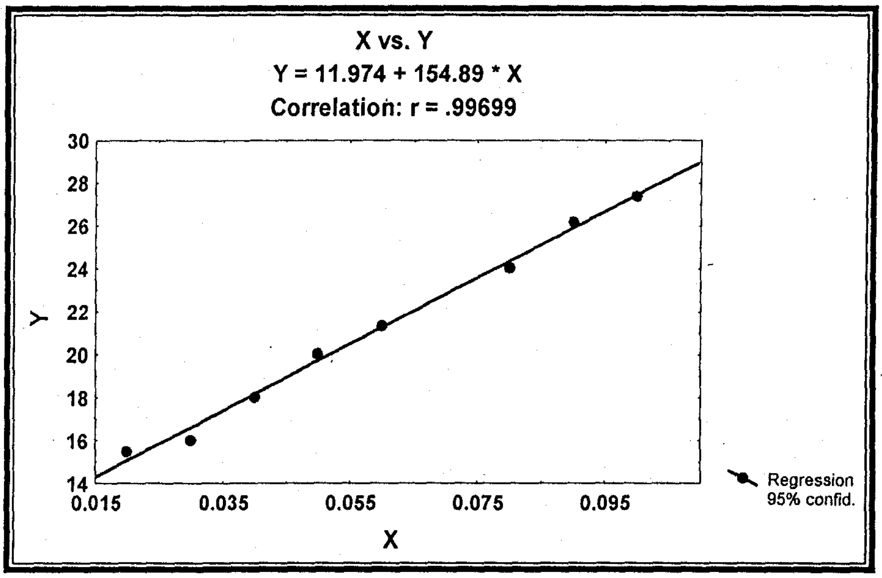


Fig.11 –OH(p)

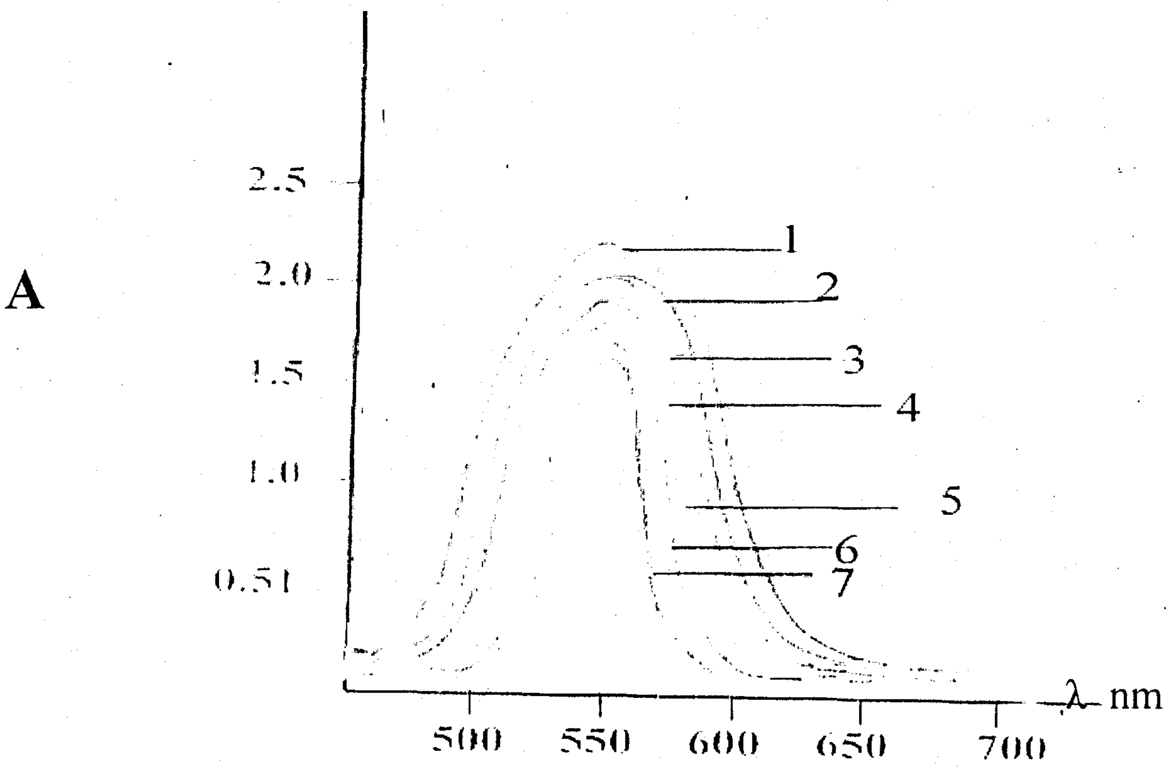
$$\lambda_{max.} = 513nm$$

Where:

Y=× 10^{-4} mole /dm^{3} =[Aa]/ODctc

X=× 10^{4} mole /dm^{3} =1/[SB]

Figurers:1-11 plots of Benesi – Hildebrands equation



Where concentrations of aliphatic Schiff base (azomethine) :
(1= 50 x 10^{-4} M) (2=45 x 10^{-4} M) (3=42 x 10 $^{-4}$ M) (4= 30 x 10 $^{-4}$ M) (5=25 x 10 $^{-4}$ M) (6= 15 x 10 $^{-4}$ M) (7 = 10 x 10 $^{-4}$ M)

Figure 12: Longer wave lengths of electromagnetic light photons and absorptions of electronic spectra of different concentrations of CTC (1) (Schiff base + acceptor) all have maximum absorptions at unique max. wave length = 536 nm

Pure and uncomplexed Schiff bases concentrations (1-7) , (10-50) 10^{-4} mole /liter & absorbs at max .wave length =395nm Pure and uncomplexed acceptor concentration =10^{-4} mole/liter & absorbs at max .wave lengths=333nm &250nm (intense) in $CHCl_3$ solvent .