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Spectral Study of some Charge Transfer Complexes Derived from Schiff base of 3- Methoxy -4-hydroxy benzaldehyde with some Electrone acceptors.

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ABSTRACT

A new series of Schiff bases were obtained by condensation of 3- methoxy -4-hydroxy benzaldehyde (vanillin) with seven aromatic amine .These bases were identified by infrared spectra and melting point . The effect of the substituents (x) on the amino ring has been studied. The charge transfer complexes (CTC) of the Schiff bases as a donor molecules with various electron acceptors as(DDQ,P-CA,O-CA,-m-Dn and PF (used for the first time as acceptor) in methylene chloride and methanol (solvent) were estimated, the physical parameters of the CT complexes were calculated by applying the Benesi –Hildebrands equation for 1:1 CT complexes .

The study also involved precipitation of one Schiff bases (1)with three electron acceptors as CT complexes and identified these complexes by IR,melting point, UV-visible and the colures.

Introduction

The study of the charge transfer complexes between several Schiff bases as electron donor and different electron acceptors such as Iodine(1), DDQ (2,3-dichloro-5,6-dicyano -1,4-benzoquinone), P-CA (2,3,5,6-tetra chloro -1,4-benzoquione), O-CA(3,4,5,6-tetra chloro-1,2- benzoquione) (2-7) and aromatic nitro compounds have been investigated by authors the equilibrium constant,the extinction coefficients of the CT complexes and the ionization potential of the acceptors were calculated. The effect of type of the substituent on the amino aromatic ring and the arene aromatic. for Schiff bases were studies by using the IR, NMR and UV- visible spectra techniques(8-10).

In this work the physical parameters of the CT complexes of seven Schiff bases derived from vanillin and some aromatic amines as electron donors with five electron acceptors in methylene chloride were calculated from their electronic spectra

Experimental

1-preparation of Schiff bases:

Seven new Schiff bases were produced from the condensation of 3- methoxy -4-hydroxy benzaldehyde (vanillin) with seven aromatic amine in absolute ethanol.

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The Schiff bases have been prepared as follows; equimolar quantities of the vanillin (1.53 gm,1 mole) and the corresponding amine (1mole)were refluxed for (10-20 minutes) at (50co) in (10-15ml) absolute ethanol. Upon cooling a crystalline product was separated, the yield was 50-60%,the solid was recrystallized from ethanol or cyclohexane table (1).

2- Preparation of CT complexes solution .

The CT complexes solution of Schiff bases were investigated with acceptors (Table (2)),(DDQ, p-CA, O-CA, PF(phenyl fluorine) and m-Dn (meta dinitro benzene) in methylene chloride(CH2Cl2). The acceptors (Fluka) are used without further purification.

The concentration of any acceptors (5x10-5M)with a certain Schiff bases as donor was kept constant in every set of solutions where the concentration of Schiff base were variable and much greater(≥5x10-5M) than the concentration of the acceptors. The measurements of the electronic spectra of the CT complexes at λmax have been recorded by double–beam Schimadzu (UV–visible) spectrophotometer UV- 1650 pc,using quartz solution cell (1 cm) path length.

Precipitation of CT complexes.

The CT complexes formed between three acceptors (DDQ,P-CA, and m-Dn) and Schiff base (1) equimoler ratio of the materials in Absolute ethanol

solvents for (30minutes), on cooling a crystalline products was separated. The product was recrystallized from cyclohexane and identified by IR spectra (were recorded on shimadzu spectrophotometer Fourier transform (FTIR) as KBr discs) and melting points measured on melting point apparalus (Electro thermal), (table 5) .

Results and Discussion .

1- Interpretation of IR Spectra

Table (3) and (4) represents the major absorption bands in the IR spectra of the studied compounds and the Schiff bases, the result shows an important variation in the stretching vibrations of certain bands as follows :

(a) The band near (3300 – 3500 cm-1) is attributed to amino group.this band shifted to the lower wave numbers or some times disappeares due to the linkage .

(b) The stretching mode of the OH band of the arene aromatis ring (vanilline group) appears as a broad or sharp near (3100-3500 cm-1) investigation reveals that the OH group is free or could be involved in hydrogen bonding(10) .

(c) The bands appeared at (1580-1624 cm-1) are related to the stretching mode of the C=N bond. The positions of the band are varied with changing the nature of the substituents(x) on the ring PhN. The band shift generally to the higher numbers with increased acceptor character of the substituent (x),in the order para > with out sub.

The order of Para substitution is in accordance with decreased polarization influence of the C=N group on the (x) subtituent .

The above data confirm that the structure of these compound are Schiff bases.

Table (4) shows the stretching mode of O-H bond for CT complex has been shifted to the higher wave number,but the stretching mode of C=N bonds shifted to the lower wave number comparing with Schiff base (1),this confirm that the structure of CT complexes is formed beside to the melting point and the change of the colour .

2 - UV –Visible

The solution of all complexes in ethylene chloride are obeyed Benesi-Hildbrand equation(11) (1) (fig-1). The solution of our Schiff bases (1-7) with DDQ,P-CA,O-CA,PF and m-Dn absorb light in the visible region Table(6-10). Fore there our Schiff base may act as an n-electron donor and the another molecules as an electron acceptors .

Equation (1) was used to calculate the extinction coefficients and equilibrium constants for our CT complexes .

[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 $\lambda_{ma\ x.}$ ε_{AD} the molar extinction coefficient and K_{CT} the equilibrium constant .

Equation (2)[12] was used to calculate the equilibrium constant Table (6-10) represent the values of EAD and KCT . The ionization potential (IP) of Schiff bases and the dissociation energies of the excited state (W) of their CT complexes were calculated using equation(12) (3) The coefficient (a) and (b) are constant for a certain acceptor(13) . From these results I and W the electron transfer originates from the same position of each Schiff bases and not affected by the other group of molecules to the acceptors, forming CT complex of the same geometry for all Schiff bases and obey Benesi–Hildbrands equatin for 1:1 complexes (the ratio of these complexes) and the only unoccupied orbital avaliable in acceptors,is the π* and the molecules Schiff bases are very rich in n-electrons,therefore,the value of the physicall parameters with the same Schiff bases similarly the type of CT complexes with acceptors are n = π* The CT complexes of seven new Schiff bases with the acceptors DDQ,P-CA, O-CA, PF and m-Dn have been investigated in methylene chloride. The solution of all complexes were obeyed Benesi-Hildbrands equation which means that the ratio of Schiff base : acceptor in every is 1:1, all complexes are n π* type (scheme 2). From Benesi-Hildbrands equation EAD and KCT of complexes were calculated . The ionization potentials of Schiff bases and the dissociation energies of the excited state of their CT complexes were also estimated .

$h\nu CT = Ip - EA - W$ …….(3)

EA is the electron affinity of the acceptor derived in terms of simple valance- bond description . Similar linear relationships have been described for complexes of many other acceptors .In general:

$h\nu CT = a\ Ip + b$ ……(4)

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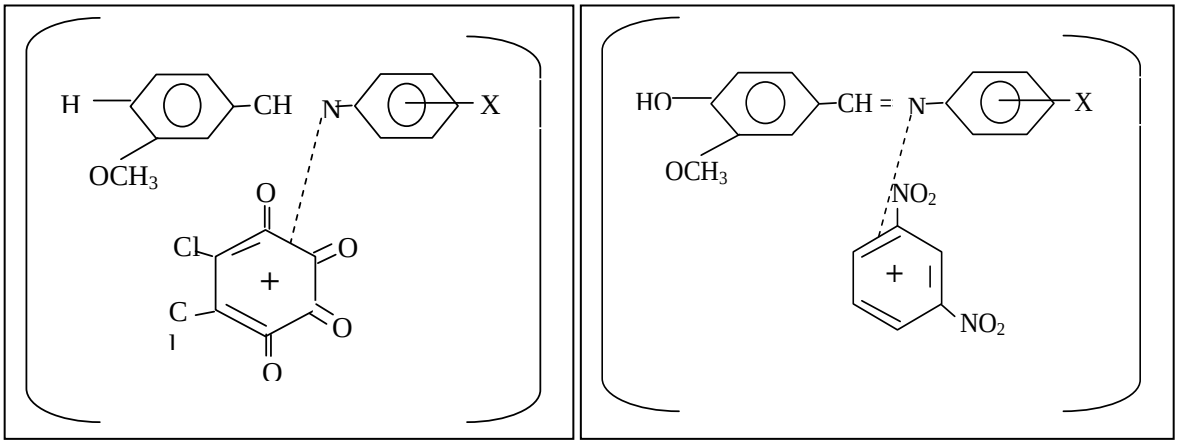
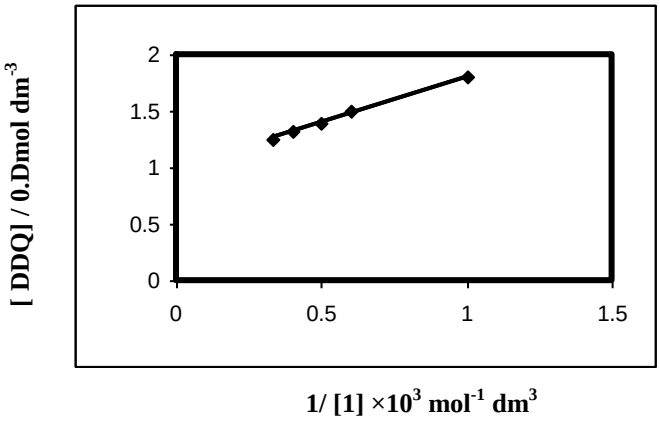


Scheme (1)



Figure(1) : Application of Benesi–Hildbrands equation for the CT Complex of Compound (1) With DDQ $(1x10^{-4})mol.dm^{-3}$ in CH_2Cl_2
λct=nm ٤٨٥εct = $100m^2 mol^{-1}$ Kct = $1333 mol^{-1} m^3$

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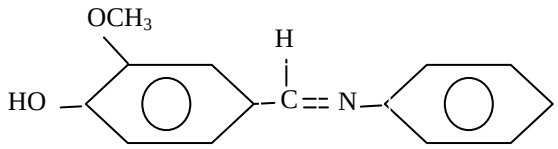
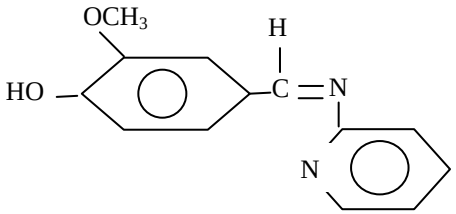
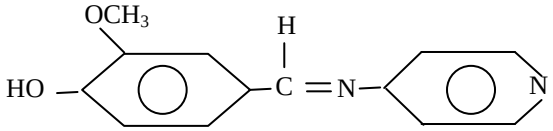
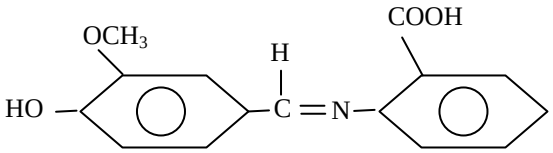
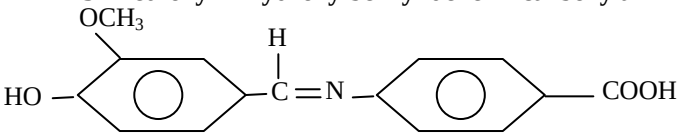
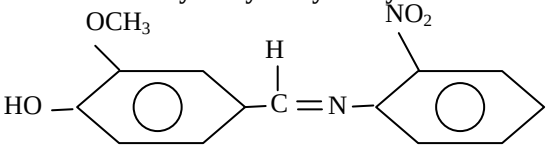
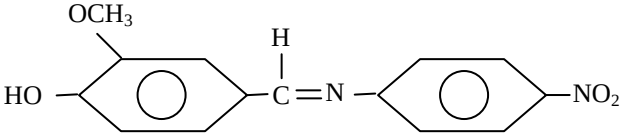
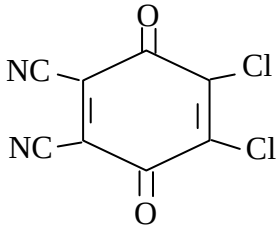
Table (1) : show the melting point and physical state of the prepared Schiff bases (donors).

No	The name and the structure of Schiff base	M.Wt	M.p /c^{o}	Physical state
1.	**3- methoxy -4-hydroxy benzylidene aniline** 	272	149-152	Yellow crystals
2.	**3- methoxy -4-hydroxy benzylidene-2-amino pyridine** 	228	70-73	Brownish crystals
3.	**3- methoxy -4-hydroxy benzylidene-4- amino pyridine** 	228	208-210	Deep red crystals
4.	**3- methoxy -4-hydroxy benzylidene-2-car boxy aniline** 	271	160-162	Yellow powder
5.	**3- methoxy -4-hydroxy benzylidene-4- carboxy aniline** 	271	205-208	Pale yellow powder
6.	**3- methoxy -4-hydroxy benzylidene-2- nitro aniline** 	272	40-43	Deep yellow crystals
7.	**3- methoxy -4-hydroxy benzylidene-4-nitro aniline** 	272	65-68	Yellow aniline

Table(2) : The Names and the Structure of acceptors

No.	Acceptor	Structures	Colour
1.	**DDQ (2,3-dichloro-5,6-dicyano benzoquinone)**		Yellow

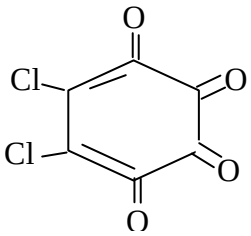
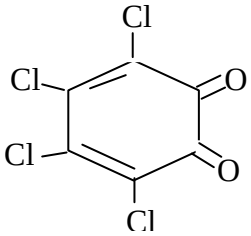
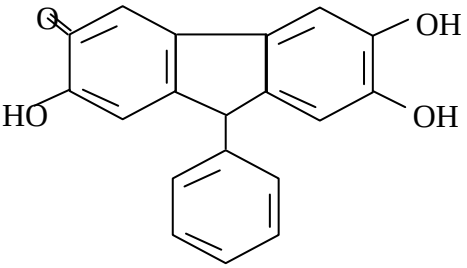
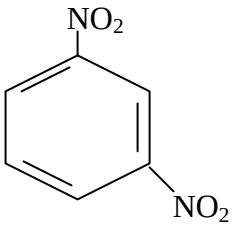
2.	**P-CA (2,3,5,6-tetra chloro 1,4-benzoquione)**		**Yellow**
3.	**O-CA (3,4,5,6-tetra chloro 1,2- benzoquione)**		**Yellow**
4.	**PF (phenylene fluorine)**		**Deep brownish**
5.	**m- Dn (meta dinitro benzene)**		**Pale yellow powder**

Table (3) : represent the melting point,colours, stretching vibration of certain band and the λ_{max} in CH_2Cl_2 for the CT complexes Schiff base (1) with three acceptors .

CT complex	M.p /c°	Colour	ν_{OH} cm^{-1}	$\nu_{C=N}$ cm^{-1}	λ_{max} nm
1 +DDQ	209-212	Yellow-Greenish	3217	1608	464
1+ P-CA	180-182	Brownish	3238	1600	405
1 +m-Dn	58-61	Brownish	3217	1587	415

Table (4):The major IR absorption peak in the spectra of compounds(1-8) .

Compound	ν_{OH} cm^{-1}	ν_{NH} cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-NO2} cm^{-1}
Vanilline	3194 (b)			
Aniline		3361-3430	1604-1627	
2- amino pyridine		3320-3484	1525-1625(shp)	
4- amino pyridine		3320-3430	1584-1645	
2- amino benzoic acid		3361-3458	1597-1650	
4- amino benzoic acid		3333-3435	1583-1665	
2- nitro aniline		3347-3472(s)	1597-1631	1248-1276(shp)
4- nitro aniline		3361-3486	1597-1631	1350(shp)

(s) = strong ; (shp) = sharp ; (b) = bonded

Table (5) : The major IR absorption peaks,measured as KBr discs, in the spectra of CT complexes(1-7) .

Schiff bases	ν_{OH} cm^{-1}	$\nu_{C=N}$ cm^{-1}	ν_{C-NO2} cm^{-1}
3- methoxy-4-hydroxy benzylidene aniline	3160(br)	1583(shp)	
3- methoxy -4-hydroxy benzylidene-o- pyridine	3300(br)	1593(s)	
3- methoxy -4-hydroxy benzylidene-p- amino pyridine	3340 (br)	1611,1580(s)	
3- methoxy -4-hydroxy benzylidene-o-carboxy aniline	3500(s)	1604,1590 (s)	
3- methoxy -4-hydroxy benzylidene-p- carboxy aniline	3157(br)	1625,1583(s)	
3- methoxy -4-hydroxy benzylidene-o- nitro aniline	3474(shp)	1624	1250,1263(shp),1298(s)
3- methoxy -4-hydroxy benzylidene-p- nitro aniline	3479(s)	1625(s),1597	1264(shp),1330(S),1333(shp

(s) = strong ; (shp) = sharp ; (br) = broad

Table (6) :the physical parameters of Schiff bases and of their CT complexes with the acceptor DDQ .

No.	λ_{CT} (nm)	K_{CT} ($mol^{-1}.m^3$)	ε_{CT} ($m^2.mol^{-1}$)	Ip (ev)	W (ev)	$h\nu_{CT}$ (ev)
1	485	1333	100	9.04	4.64	2.47
2	507	13082	769	8.88	4.59	2.36
3	375	300	758	10.00	4.95	3.19
4	532	3697	435	8.72	4.54	2.25
5	471	1667	147	9.14	4.67	2.54
6	377	962	192	10.00	4.94	3.17
7	380	187	100	9.95	4.91	3.15

Table (7) :the physical parameters of Schiff bases and of their CT complexes with the acceptor P-CA

No.	λ_{CT} (nm)	K_{CT} ($mol^{-1}.m^3$)	ε_{CT} ($m^2.mol^{-1}$)	Ip (ev)	W (ev)	$h\nu_{CT}$ (ev)
1	400	1931	125	9.12	4.76	2.99
2	439	1360	476	9.88	4.84	2.72
3	346	3496	769	10.00	4.86	3.46
4	382	4761	714	9.31	4.78	3.13
5	372	3401	714	10.10	4.87	3.22
6	380	14035	175	9.39	4.79	3.15
7	370	4395	153	9.30	4.78	3.23

Table (8) :the physical parameters of Schiff bases and of their CT complexes with the acceptor O-CA

No.	λ_{CT} (nm)	K_{CT} ($mol^{-1}.m^3$)	ε_{CT} ($m^2.mol^{-1}$)	Ip (ev)	W (ev)	$h\nu_{CT}$ (ev)
1	428	9410	454	9.18	5.87	2.79
2	400	1360	416	10.30	5.19	2.99
3	388	13605	952	9.49	4.95	3.08
4	380	16095	917	10.10	5.85	3.15
5	350	1325	243	10.00	5.45	3.42
6	370	1628	158	9.82	5.00	3.25

Table (9) :the physical parameters of Schiff bases and of their CT Complexes with the acceptor PF

No.	λ_{CT} (nm)	K_{CT} ($mol^{-1}.m^3$)	ε_{CT} ($m^2.mol^{-1}$)	Ip (ev)	W (ev)	$h\nu_{CT}$ (ev)
1	450	7440	312	10.40	6.65	2.66
2	526	1851	111	10.00	6.48	2.27
3	490	1481	666	9.80	6.35	2.44
4	496	3431	425	10.00	6.46	2.41
5	496	1611	588	10.00	6.46	2.41
6	493	2380	333	9.96	6.42	2.43
7	436	1709	153	10.00	6.47	2.74

Table (10) :the physical parameters of Schiff bases and of their CT complexes with the acceptor m-Dn

No.	λ_{CT} (nm)	K_{CT} ($mol^{-1}.m^3$)	ε_{CT} ($m^2.mol^{-1}$)	Ip ev)	W (ev)	hv_{CT} (ev)
1	420	9090	400	11.40	7.22	2.85
2	456	3333	166	10.90	6.94	2.62
3	410	1005	869	11.60	7.31	2.92
4	423	6067	625	11.40	7.20	2.83
5	371	1033	775	12.30	7.68	3.22
6	436	1688	476	11.20	7.10	2.74
7	381	3003	222	12.10	7.58	3.14

دراسة طيفية لبعض معقدات انتقال الشحنة الجديد المشتقة من قواعد شيف لمركب ٣-ميثوكسي-٤-هيدروكسي بنزلديهايد مع بعض المستقبلات الإلكترونية

عبد الرحمن خضير عبد الحسين ليلى عبد الرحمن جبر

الخلاصة

تم في هذه الدراسة تحضير مجموعة من قواعد شيف الجديدة المشتقة من تكثيف مركب ٣-ميثوكسي-٤-هيدروكسي بنزلديهايد (الفانلين) مع سبعة أمينات اروماتية، تم تشخيص هذه القواعد باستخدام طيف الأشعة تحت الحمراء وقياس درجات الانصهار، وتضمن البحث دراسة تأثير المعوضات على هذه القواعد في حزم الأشعة تحت الحمراء للحلقة الاورماتية القريبة من النتروجين لهذه القواعد. كما تضمن البحث تحضير معقدات انتقال الشحنة بهيئة محاليل لهذه القواعد مع مجموعة من المستقبلات الإلكترونيةDDQ, p-CA, O-CA, PF (ولأول مرة يستخدم كمستقبل) وm-Dn في مذيب كلوريد الأثلين،و بتطبيق معادلة بنسي- هلدبراند أمكن أيجاد بعض المتغيرات الفيزيائية لهذه القواعد والمعقدات. كما تضمن البحث ترسيب أحدى هذه القواعد مع ثلاثة مستقبلات الكترونية وتم تشخيصها بطيف الأشعة تحت الحمراء وقياس درجات الانصهار لها ومقارنة طيف الأشعة فوق البنفسجية لها مع محاليلها في المعقدات.