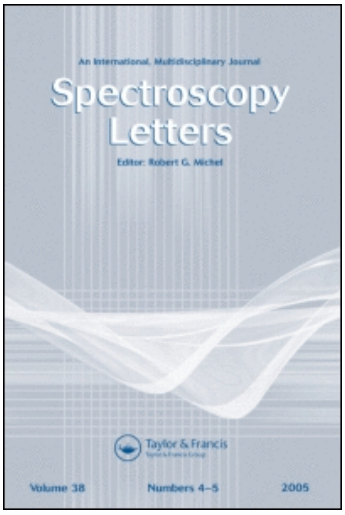

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"Charge transfer Complexes of Indolyldiene Aniline derivatives with p-benzoquinone derivatives"

M. Gaber[ab]; H. A. Dessouki[c]; E. H. Hossani[c]
[a] Tanta University, Tanta, Egypt [b] Chemistry Department, Faculty of Science, Sana'a University Sana'a, Republic of Yemen [c] Chemistry Department, Faculty of Science Zagazig University, Banha Pranch, Banha, Egypt

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"Charge transfer Complexes of Indolyldiene Aniline derivatives with p-benzoquinone derivatives"

By

M.Gaber*,H.A. Dessouki and E.H. Hossani
Chemistry Department -Faculty of Science
Zagazig University- Banha Pranch Banha- Egypt
* Tanta University -Tanta- Egypt.

Charge transfer (CT) complexes of p-benzoquinone derivatives with Indolyldiene aniline derivatives have been prepared and investigated by Elemental analysis, IR, ^{1}H-NMR and electronic absorption spectroscopy. The spectral changes revealed that acidic acceptors form complexes with $\pi - \pi^*$ electronic interaction and proton transfer while non-acidic acceptors yield complexes having $\pi - \pi^*$ transition only. The formation of 1:2 (D:A) complexes is also ascertained. The ionization potential and electron affinity are determined from the electronic absorption spectra for both the donors and acceptors respectivily.

Introduction

The formation of molecular complexes of the charge transfer CT type between electron quceptors such as p-benzoquinones and electron donors was the subject of a vast number of interesting investigations.

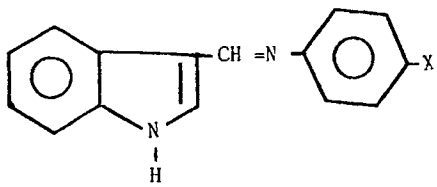
* : Present address: Chemistry Department Faculty of Science, Sana'a University Sana'a, Republic of Yemen.

For schiff bases of aniline with benzaldehydes derivatives 1:1 or 1:2 (D:A) complexes are formed irrespective of the type of bonding in the molecular complexes[1-5].

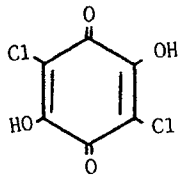
In the present investigation, the CT complexes formed through the interaction of some Schiff bases derived from Indolyldiene aniline derivatives with some p-benzoquinone derivatives are investigated using Elemental microanalysis, IR, ^{1}H-NMR and electronic absorption spectroscopy.

Experimental

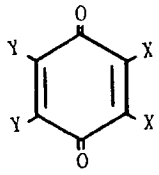
All compounds used in the present work were B.D.H. pure grade chemicals. The donors used have the general structural formula:-



where x : p-O CH_3 (a), p-OH (b) and H (d). The acceptors used have non acidic character- [2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ), chloranil (CHL) , Bromanil (BRL)-and Iodanil(IDL).] - and acidic character as chloranilic acid (CHLC).



(CHLC)



where : X = y = Cl (CHL)

= Br (BRL)

= I (IDL)

x = Cl, y = C = N (DDQ)

The preparation of the CT complexes and the working procedures are the same as described previously[6-8]. The IR spectra were recorded on Unicam sp. 1000 infrared spectroscopy, the electronic absorption spectra were recorded on Perkin Elmer spectrophotometer (3B) using Nujol mull technique[9].

The ^{1}H-NMR spectra were obtained on a Varian E M 390-(90 MHZ) NMR spectrometer in deutrated DMSO as solvent using TMS as intenal stander.

Results and discussion

The results of elemental mincro analysis of some CT complexes under investigation are given in Table (1). The data indicate the formation of 1:2 (donor : acceptor) complexes, the spectral characteristics of the CT complexes under investigation are discussed in the following:-

(A) Molecular complexes involving electron and proton transfer:-

i) IR spectra:-

The spectra of these compounds show a new group of bands within the 2900-2400 cm^{-1} range which corresponds to $\nu^{+}_{=NH}$ band; this new group is formed through the transfer of a proton from the phenolic OH group of chloranilic acid (CHLC) to the basic C = N center of the donor. The $\nu_{C=O}$ bands display a more or less identical behaviour in CT complex formation. The three bands in the spectrum of (CHLC) are reduced to two bands due to the destruction of the intermolecular hydrogen bond; these bands exhibit

Table 1: Microanalysis of the CT complexes of donors a,b and c with different acceptors

Comp. No.	molecular formula	C% Calcul.	C% fou.	H% Calcul.	H% fou.	N% Calcul.	N% fou.	X% Calcul.	X% fou.
		Complexes of donor (a)							
DDQ	$C_{32}H_{14}N_6O_5Cl_4$	54.55	53.82	2.00	1.98	11.93	11.68	20.17	19.93
CHL	$C_{28}H_{14}N_2O_5Cl_8$	46.09	46.46	1.84	1.76	3.65	3.36	37.07	36.96
CHLC	$C_{26}H_{18}N_2O_9Cl_4$	52.01	51.92	2.62	2.32	4.05	3.98	20.52	19.84
BRL	$C_{28}H_{24}N_2O_5Br_8$	32.11	31.84	1.26	1.15	2.407	2.00	57.00	56.86
IOL	$C_{28}H_{14}N_2O_5I_8$	24.04	23.96	0.94	0.88	1.87	1.78	67.80	66.98
		Complexes of donor (b)							
CHLC	$C_{27}H_{16}N_2O_9Cl_4$	49.50	48.98	2.46	2.24	4.24	3.86	21.71	20.87
BRL	$C_{27}H_{12}N_2O_4Br_8$	29.90	29.02	1.12	0.98	2.58	2.45	59.01	58.63
		Complexes of donors (c)							
DDQ	$C_{29}H_{12}N_6O_4Cl_4$	55.19	54.62	1.79	1.68	12.46	11.86	21.07	20.76
CHLC	$C_{27}H_{16}N_2O_8Cl_4$	54.20	53.83	2.35	1.96	4.08	3.95	20.70	19.95
IDL	$C_{27}H_{12}N_2O_4I_8$	24.90	24.60	0.81	0.78	1.88	1.76	68.08	67.92

Table (2): IR spectra of CT complexes for donors III_a, III_b and III_d with nonacidic acceptors.

comp	Ratio	m.p°C	colour	γ CH out	-NC str	C≡N str	C=O str	-N-H aryl	ν_{OH} str
free	(A)		IV (DDQ)			2235	1674		
III_a	free			735,790	1620,1650			1240,1290	
	1:1	110	brown	755,790	1580	2220	1650	1235	
	1:2	125	brown	760,800	1650	2210	1700	1260	
III_b	free			740,810	1610,1630			1240	3200,3320
	1:1	143	darkbrown	760,790	1590	2260	1650	1250	3260,3400
	1:2	140	darkbrown	750,780	1580	2260	1650	1210,1280	3200,3400
III_D	free			750,780	1610,1635			1240,1290	
	1:1	115	red	750,780	1575,1610	2220	1640	1240	
	1:2	120	red	750,780	1650	2230	1700	1250,1290	
			V (CHL)						
free	(A)						1695,1682		
III_a	1:1	183	red	760,800	1650		1700	1255	
	1:2	140	red	755,830	1650		1700	1255	
III_b	1:1	196	brown	755,790	1650		1700	1250	3200,3300 broad
	1:2	200	brown	750,790	1650		1700	1260	3180,3260
III_D	1:1	134	grey	755,790	1650		1700	1250,1300	
	1:2	125	buff	750,790	1650		1700	1250,1300	

a shift to lower wavenumbers (Table 2) as a result of the increased π-electron density on the ring of the acceptor part of the CT complexes, a behaviour which is commonly observed[6] with the CT complexes involving proton transfer.

The γ_{CH} band of the donor is shifted to lower wave number, a behaviour which is characteristic of the π-π^* CT interaction[6,12]. The shifts of the γ_{CH} bands of the benzal Rings in the 1:1 complexes account for a higher charge migration from this ring to the $-C=\overset{+}{N}-H$ center in the CT complex compared with the free state of donors, which results from the existence of the positive charge on the nitrogen atom.

ii) Electronic absorption spectra:-

The electronic absorption spectra of the CT complexes belonging to this class of complexes are characterized by one CT band within the 400-550 nm. range, the existence of one band denotes that π- π^* interaction contributes to bonding in these CT complexes; n-π^* interaction is absent due to the blocking of the nitrogen lone pair through the proton trnasferred from the acceptor. There-fore the electronic absorption spectra of the CT complexes of donors (a),(b) and (d) with (CHLC) in ratio 1:1 and 1:2 (donor: acceptor) show another weak band at 500-550 nm corresponding to n-π^* transition. This is based on the fact that the formation of the acceptor center-C=N-H in the 1:1 and 1:2 complexes would inhibit the proton migration of the second OH-group, via one proton transfer from (CHLC) to the N-atom of azomethine group on the formation of 1:1 and 1:2 complexes.

This assumption is supported by calculating the energy of the π-π^* (HOMO - LUMO) CT interaction (table 3) E_{CT} using the relation given by

Table (3): IR spectra of CT complexes for donor III [a,b and d] with acidic and nonacidic acceptors.

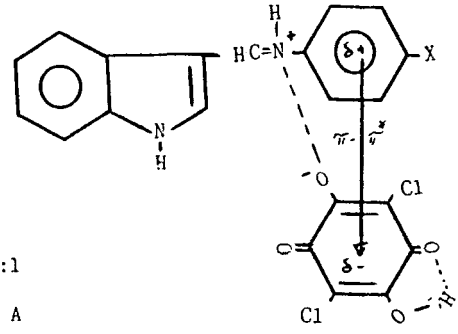
comp.	ratio	m.p°C	colour	γ -CH out	N=C str	ν_{OH} str	-NH str	C=O str .	-N-H aryl
free	(A)				chloranilic acid.	3235,3170		1670,1637	
III_a	free			735,790	1620,1650				1240,1290
	1:1	113	palebrown	760,840	1620	3200	2950,3100	1650,1620	1280
	1:2	125	palebrown	750,780	1550,1610	3220	2900,3240	1640,1600	1280
III_b	free			740,810	1610,1630		3320,3200		1240
	1:1	140	violt	760,850	1650	3300	3200,3360	1650	1260
	1:2	165	violt	750,850	1640	3280	3240,3340	1650	1300
III_D	free			750,780	1610,1635	3160,3300			1240,1290
	1:1	130	grey	760,780	1580	3200,3285	3250	1650	1250,1300
	1:2	120	grey	750,850	1590	3200,3300	3260	1640	1290
free	(A)			VII (BRL)				1640,1680	
III_a	1:1	150	red	760,790	1650			1650	1250
	1:2	165	red	765,790	1690			1690	1260
III_b	1:1	170	brown	760,790	1690	3180,3380		1690	1250
	1:2	160	brown	760,830	1690	3200,3320		1685	1250
III_D	1:1	130	redishbrown	760,790	1690			1680	1250
	1:2	125	paleyellow	770.790	1690			1688	1250
free	(A)			VIII (IDL)				1660,1680	
III_a	1:1	260	brown	770,830	1650			1580	1260
	1:2	255	brown	790,840	1670			1580	1250
III_b	1:1	270	negrow	790,840	1650	3200,4300		1620	1250
	1:2	265	negrow	790,830	1670	3200,3500		1260,1635	1250
III_D	1:1	240	brown	760,790	1680			1650	1250
	1:2	225	brown	765,790	1690,1710			1650	1250

Briegleb[10,11]. The values calculated for CT complexes with (CHLC) amound to 2-24-3.0 ev corresponding to λ_{max} of 490-550 nm which is in good agreement with the experiment values 2.35-3.08 ev.

iii) ^{1}H-NMR spectra:-

The ^{1}H-NMR spectra of the complexes, in comparisone with those of the free components reveal shifts of the signals, due to the donor part to lower fields whereas those of the acceptor are shifted to higher fields.

This results from the $\pi-\pi^*$ interaction leading to increased π- electron density on the accptor and its decrease on the donor.



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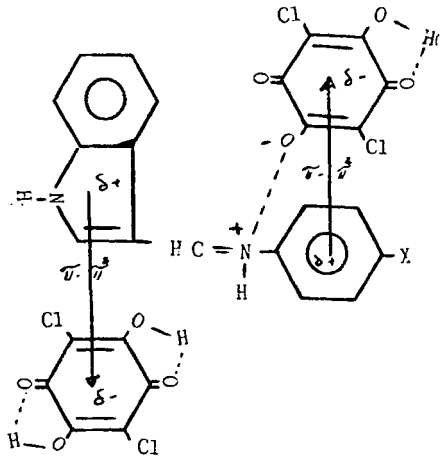


Table (4): The H^1 nmr spectra for some CT complexes of donors IIIa, IIIb and IIId with acceptors.

Signals of acceptor part			Signals of donor part								
Ratio	H^3	H^6	H^1	H^2	H^3	H^4	H^5	H^6	=CH	$\overset{\diagdown N \diagup}{\underset{H}{}}$	$=^{+}N-H$
free donor IIIb			12.0	6.8	7.2	8.65	8.25	8.35	6.4	7.85	
complexes with A (IV)					(DDQ)						
1:1			13.2	6.6	7.1	8.4	8.15	8.2	6.3	7.45	
1:2			12.4	7.6	7.45	9.8	8.1	8.3	6.8	7.85	
complexes with A (V)					(CHL)						
1:1			12.3	7.0	7.2	9.9	8.0	8.2	6.6	7.5	
1:2			12.2	6.9	7.25	9.9	8.0	8.2	6.7	7.45	
free (VI)	8.9	8.7			(CHLC)						
1:1		8.5	12.5	7.2	7.5	9.9	8.0	8.2	6.8	7.8	7.6
1:2		8.45	12.2	7.25	7.5	9.95	8.2	8.4	6.9	7.35	7.7
complexes with A (VIII)					(BRL)						
1:1			12.3	6.9	7.3	10.0	8.2	8.35	4.7	7.6	
1:2			12.2	6.9	7.35	10.0	8.2	8.35	5.3	7.8	
complexes with A (VIII)					(IDL)						
1:1			12.2	6.8	7.3	10.0	8.1	8.3	3.8	7.5	
1:2			12.0	6.9	7.25	9.9	8.0	8.25	3.55	7.5	
free donor IIIa			3.9	7.2	7.35	8.5	7.6	8.1	7.0	8.9	
A (VI) 1:1			3.8	7.25	7.6	10.0	7.95	8.2	8.35	9.45	6.2
1:2			3.8	7.2	7.3	10.0	7.7	8.3	7.15	8.1	7.1
free donor IIId			7.2	7.45	7.6	8.55	8.0	8.5	7.3	8.7	
A (VI) 1:1			7.3	7.3	7.65	10.0	8.15	8.3	7.7	8.35	7.5
1:2			7.3	7.3	7.6	10.0	8.15	8.2	7.6	9.1	9.6

where X : p-OCH_3(a), p-OH (b) and p-H (d).

The ^{1}H-NMR spectra of the CT complexes involving proton transfer exhibit a broad signal within the 3-7 ppm range (Table 4) which is not present in the spectra of the free components; this signal of ^{1}H-intensity can be assigned to the new center $= \overset{+}{\underset{1}{N}}-H$, which is absent in the spectra of the free donors and acceptors. This is supported by the fact that the signal due to the OH group is more observed for 1:1

and some 1:2 complexes, while for 1:2 complexes this signal appears at 8-10 ppm due to free OH group of the second molecule of (CHLC).

(B) Molecular complexes involving electron transfer only:-

Since the acceptor used is deprived of an acidic center, the only possible way of CT complex formation would be electron transfer either from the π-electron of the aromatic rings or the n-electron of the azomethine linkages.

i) IR spectra:-

The IR spectra of the CT complexes compared with those of the simple components reveal an apparent shift of the γ_{CH} bands of the donor are shifted to higher values.

This shift is observed with CT complexes involving π-π^* intermolecular (HOMO $\longrightarrow$ LUMO) electron transfer from highest occupied π-level in the donor molecule to the lowest unoccupied level in the acceptor[12]. The shift of the γ_{CH} bands of the anilino and Indolyl rings display an identical behaviour as in the case of CT complexes with (CHLC), revealing that the electron transfer to the acceptor in the 1:1 complex would originate also from the anilino ring. Such CT interaction leads to obvious shifts in the C=O bands of the acceptor (table 2).

ii) The electronic absorption spectra:-

The electronic absorption spectra of some CT complexes under investigation (DDQ), (CHL) , (BRL) and (IDL) display a single CT band within the 400-550 nm range (Table 3) corresponding to the π-π^* intermolecular interaction; the n-π^* type if involved in the CT interaction , would be of low contribution to complex formation or entirely absent.

Table (5): The experimental values of E_{CT} for some complexes of indolyl period.(III).

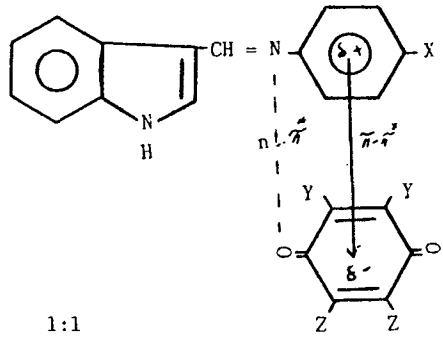
D	Ratio	a p-OCH_3		b p-OH		d p-H	
		λ_{CT}	E_{CT}	λ_{CT}	E_{CT}	λ_{CT}	E_{CT}
IV	1:1	488,452	2.55,2.75	480,445	2.59,2.80	485,446	2.56,2.79
	1:2	485,450	2.56,2.70	488,450	2.55,2.76	486,440[b]	2.56,2.83
V	1:1	480,440	2.59,2.83	485,450	2.56,2.76	487,453	2.55,2.76
	1:2	485,450	2.56,2.76	489,440	2.54,2.83	483,445	2.58,2.80
VI	1:1	485,450	2.56,2.76	480,454	2.59,2.74	488,452	2.55,2.75
	1:2	480,445	2.59,2.80	485,450	2.56,2.76	482,450	2.58,2.76
VII	1:1	490,450	2.54,2.76	486,448	2.56,2.78	485,455	2.56,2.73
	1:2	485,442	2.56,2.81	487,450	2.55,2.76	482,450	2.58,2.76
VIII	1:1	480,445	2.59,2.80	478,430	2.55,2.89	485,450	2.56,7.76
	1:2	485,450	2.56,2.76	489,440[b]	2.54,2.83	483,448	2.58,2.78

This assumption is supported by calculating the energy of the π- π^* CT interaction (E_{CT}) using the relation given by Briegleb[10,11]

$$E_{CT} = I_p - (E_A + C)$$

The values calculated for CT complexes with acceptor (DDQ) and (CHL) amounts to 2.54-2.90 ev corresponding to λ_{max} of 480-500 nm which is in good agreement with the experimental values (450-520 nm). Plot of E_{CT} as a function of I_p of the donors (a),(b) and (d) are approximately linear with ronghly identical slopes but varied intercepts.From the intercepts, the electron affinities of the acceptors under investigation are determined and amount to 1.95 ev (DDQ) , 1.37 ev (CHL), 1.41 ev (BRL) , 1.69 ev (IDL)

and 1.10 ev (CHLC). The values of E_A determined from the plot is in good agreement with the values calculated from Brieglob's equation[10] 1.28 ev (DDQ), 1.10 ev (CHL), 1.25 ev (CHLC), 2.0 ev (BRL) and 1.76 ev (IDL).



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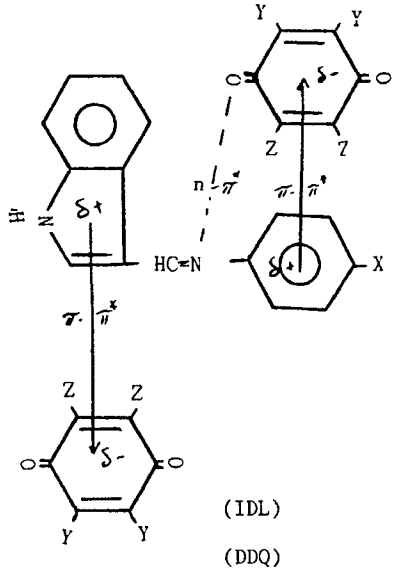

(IDL)

(DDQ)

iii) ^{1}H-NMR spectra:-

The ^{1}H-NMR spectra of the CT complexes with DDQ , CHL, BRL and IDL compared with those of the simple constituents reveal a shift of the signals due to the protons of the acceptor to higher fields, while there of the donor are shifted to lower fields. This behaviour is the common one for complexes of the $\pi - \pi^*$ type, resulting in a lower shielding effect on the protons of the donor Schiff bases and its increase on these of the acceptors molecule. The shift of the signals due to proton of the anilino part are higher than those of Indolyl which is in confirmity with the results of the IR spectra.

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