CHARGE-TRANSFER COMPLEXES OF QUINALDINE-ARYLIDEN SCHIFF BASES WITH FLUORANIL AND 2,4-DINITROFLUOROBENZENE

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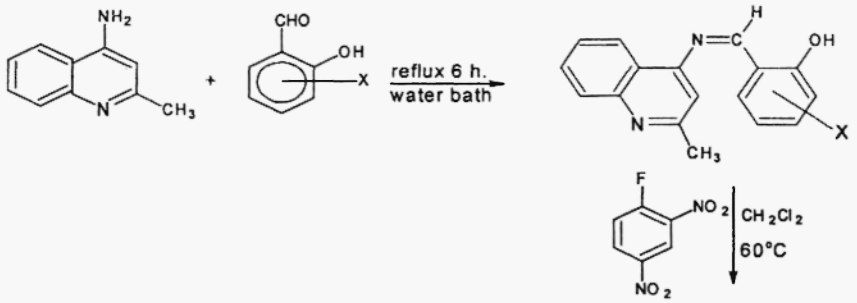
Abstract: Molecular complexes of charge transfer of some 4-(2-hydroxy-4' -substituted benzyldene amino)-2-methyl quinoline with fluoranil and 2,4-dinitrofluorobenzene have been investigated by IR, ^{1}H-NMR, electronic absorption and ESR spectroscopy.



Product [CT Complex]

The stoichiometry and apparent formation constants of the complexes formed were determined by applying the conventional methods, the role of the molecular structure of the cómplexes as well as the equilibrium constants (K), Oscillator strength (*f*), dipole moment (μ,) and free energy (ΔG*) are elucidated.

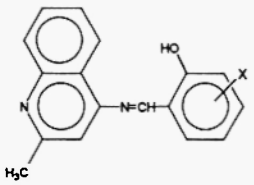
Introduction:

π-π* Molecular complexes of (2.2) paraclophane derivatives with tetracyanoethylene, 2.,3-dichloro-5,6-dicyanobenzoquinone and chloranil were studied. Molecular complexes ofcyclophanes charge transfer complexes with flouranil were studied spectrophotome-trically[1]. Intermolecular charge-transfer complexes of some heteroaromatic N-oxides with halogenated benzoquinones were investigated spectrophotometrically[2]. Molecular compounds of halogen derivatives of benzoquin-ones with donor molecules were the subjects of several interesting studies. These studies deal mainly with the determination of the electron affinities of the acceptors or the ionization potential of the donor molecules[3-6] and the investigation of the charge transfer interaction within the complex molecule[7]. The molecular complexes of some hydroxy aromatic Schiffs bases with 2,3-dichloro-5,6-dicyanobenzoquinone and chloranilic acid were prepared and investigated[8]. Charge-Transfer (CT) complexes of p-benzoquinone derivatives with indolyldiene aniline derivatives were prepared and investigated[9].

In the present article is concerned with the study of the behaviour of aryl schiff bases which act as donor, towards complexation with benzoquinones and nitrobenzene as Ti-acceptors. The stoichiometry of the charge-transfer complexes under investigation were elucidated.

Experimental:

Fluoranil (FRL) and 2,4-dinitrofluorobenzene (DNFB) are Aldrich grade. The solvent used (methylenechloride) was purified following the previous[10] method, dried and distilled, the aryl schiff bases was prepared according to Vogel, and have the following formula:



where: X = - H(I), p-OH (II), p-OCH3 (III) and 3,5-di-Cl(IV)

For determining the stoichiometry of CT complexes using the conventional continuous variation method (Job's method[11], stock solutions ($3x10^{-2}$ molar) of donor and acceptors were prepared. While for determining the stability constant of formation (K) from Bensi-Hildebrand equation[12] the concentration of acceptors was $3x10^{-2}$ mole, while those of the donor ranged from $1x10^{-2}$ to $8x10^{-2}$ mole. The electronic spectra of the complexes were measured in methylene chloride at 25 °C, 30 °C, 35 °C, 40 °C and 45 °C.

The preparation of the molecular complexes and the working procedure are the same as described previously[9]. The IR spectra were recorded on Perkin-Elmer 683 infrared spectrophotometer, the ^1H NMR spectra were obtained by the aid of the varian EM-390-90 MZ-NMR spectrometer and electron spin resonance (esr) spectra were recorded on a varian E-g X-band spectrometer equipped with an E 101 microwave bridge.

Results and discussion:

Taking into consideration the presence of an electron donating group in the electron donating group in the electron donor system under investigation on mixing the methylene chloride solutions of the donor and acceptors different colours characteristic of charge transfer transitions were observed. This fact was further supported by measuring the absorption of these solutions, which gave characteristic broad bands absorbed in the visible region, in which neither the donor nor the acceptor separately absorb. On the other hand, according to the reported electron affinity (E_A) values of these Ti-acceptors[13] Values of the association constants (K) values of the CT complexes together with the molar extinction coefficient (ε) were determined by Bensi-Hildebrand equation[14].

$$[A]+[D]=\frac{\varepsilon l[A][D]}{[d]}-\frac{1}{K}$$

Where [A] and [D] are the initial molar concentration of acceptor and donor respectively, (L) the length of light path in cm and (d) the optical density. They

values of(K) are determined from the gradient and negative intercept of the linear plot of [A] + [D] against [A][D]/d (Fig.l). This method enables one to determine K and c independently for the CT complexes under the condition of constant [A] and tabulated in (Table 1). From the relation between In k and (I/T) deduced the values of -ΔH k cal/mole for these charge-transfer complexes, also from computed K values from above were used to calculate -ΔG* values according to equation[14].

$$-\Delta G^* = -RT \ln k$$

The complexes are found to have -ΔG* equal to (6.5-16.6) kcal/mole indicating the very weak nature of the complexes and spontaneous reaction and agreement with the general trend that -ΔG* values increases as the electron affinity of the acceptor increases (Table 1). Spectral determination of equiligrium constants and molar extinction coefficient for chage transfer complexes of (I), (II) and (III) with (DNFB) (Fig. l).

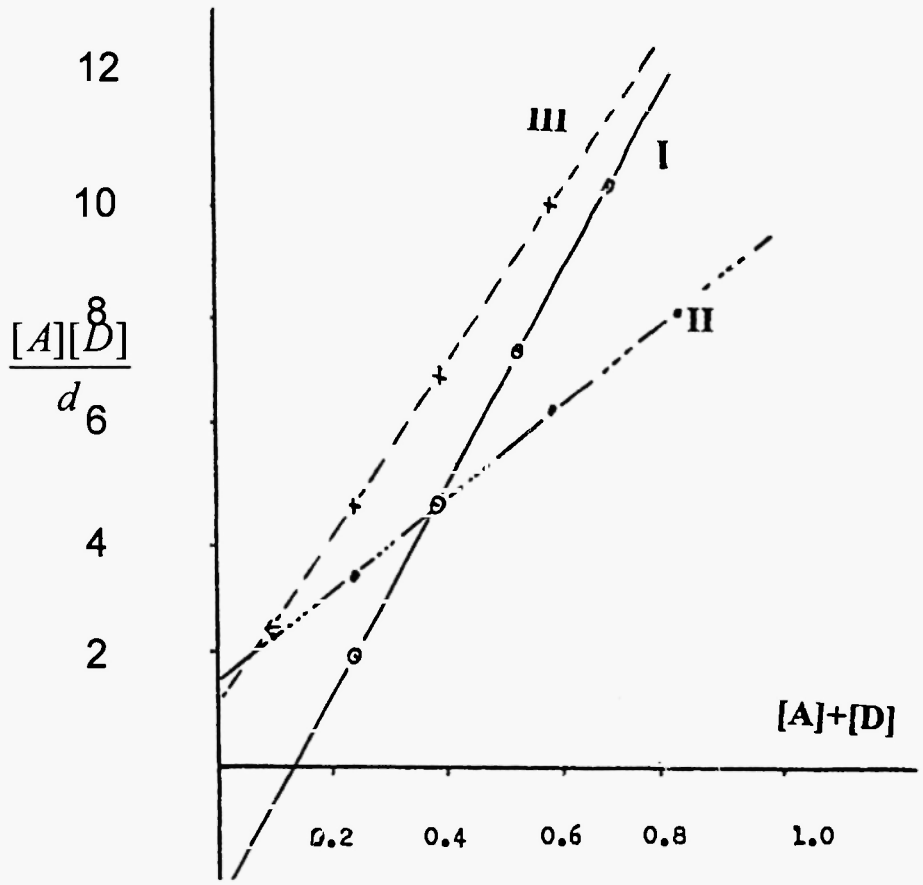


Fig. (I) Spectral determination of equilibrium constants and molar extinction coefficients for CT complexes of (I), (II) and (III) with (DNFB).

The stoichiometry of the CT complexes between the aryl Schiff bases with fluoranil and 2,4-dinitrofluorobenzene are found to be 1:1 and 1:2. This result was confirmed by application of Job's method[11]. For continuous variation method which gave symmetrical curve with maxima of a mole fraction of 0.5. In addition the straight line of Bensi-Hildebrand method utilized for determination of K and ε

values further supports this stoichiometric ratio, the energy of the CT transitions (E) reported in (Table 1) have been calculated by using Briegleb's equation[5]. Further information about the relative electron affinities of the acceptors could be inferred from the E values. Determined by making use of both the Bensi-Hilderbrand and Job (Continuous variation) methods. Also, the effect of thermodynamic parameters on the stability of such types of complexes were discussed.

The molecular compounds of the aryl Schiff bases with fluoranil and 2,4-dinitrofluorobenzene are prepared and investigated by IR, ^{1}H-NMR, electronic absorption and ESR spectroscopy.

Table (1): The association constants (K), the transition energy and thermodynamic parameters of CT complexes with fluoranil (FRL) and 2,4-dinitrofluorobenzene (DNFB).

Comp.	IP	T°C	KL. Mol^{-1}	-ΔH (K.cal/mol)	-ΔG* (K.cal/mol)	ε L/mol. Cm	ECTev
			FRL DNFB	FRL DNFB	FRL DNFB	FRL DNFB	FRL DNFB
		25	4.82 5.44				
		30	5.76 6.82				
I		35	6.60 7.40	5.70 6.30	6.30 7.46	580 610	2.80 2.04
H		40	6.80 7.60				
		45	7.40 8.20				
		25	11.40 12.10				
		30	14.50 15.64				
11		35	16.40 17.80	8.40 9.50	14.6 16.61	850 920	1.95 2.36
P-OH		40	21.60 23.61				
		45	23.10 24.19				
		25	3.80 4.78				
		30	3.90 4.84				
III		35	4.60 4.74	3.70 4.90	5.30 6.50	440 490	1.04 1.97
P-		40	5.50 6.44				
OCHs		45	6.30 7.24				
		25	7.50 8.60				
		30	7.60 8.82				
IV		35	8.40 9.40	5.60 6.80	10.6 11.8	660 735	1.95 2.17
2,4		40	8.65 9.62				
di-Cl		45	9.70 10.42				

Molecular charge-transfer complexes:

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

Interaction involving electron transfer only:

This class of complexes are formed using acceptors fluoranil and 2,4-dinitrofluorobenzene; the IR spectra of these complexes (Table 2) display obvious shifts in the position of most bands compared to the spectra of the components. The bands due to the various vibrations of the acceptor part are shifted to lower wavenumbers while those of donor part reacquire a counter shift.
The shift of the γ CH bands of the donor to higher wave numbers is considered to be a criterion for a CT interaction of the π-π*.

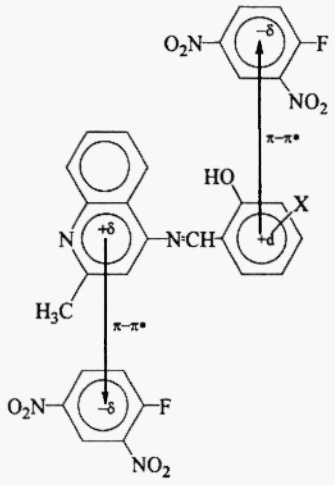
Table (2): IR, ^{1}H-NMR and ESR spectra for charge transfer complexes

Comp.	γ CH	υ sym NO_2	υ asym NO_2	υC=0	υOH	^{1}H-NMR			g_{eff}
						δCH	δCH_3	δOH	
Complexes with fluoranil (FRL)									
Free (A)				1680-1740	-	-	-	-	-
I(H)	890-910	-	-	1690-1750	3180-3210	6.5	4.9	10.3	2.9080
11 P-OH	870-840	-	-	1780-1800	3150-3260	6.4	5.6	11.0	1.9840
III P-OCH_3	925-907	-	-	1750-1784	3340-3280	6.7	5.8	9.8	2.9040
IV 3.5 di-Cl	915-940	-	-	1760-1700	3100-3240	6.2	5.3	10.5	1.9652
Complexes with 2,4-dinitrofluorobenzene (DNFB)									
Free (A)	810-840	1320	1560	-	-	8.4	-	-	-
1(H)	790-805	1330	1685	-	3250	7.6	5.2	9.5	2.9060
II P-OH	820-825	1355	1675	-	3340	7.8	5.4	9.8	1.9860
III P-OCH_3	840-855	1340	1590	-	3360	8.1	5.1	9.4	2.8900
IV 3.5 di-Cl	780-810	1350	1580	-	3180	7.4	4.8	9,1	1.9740

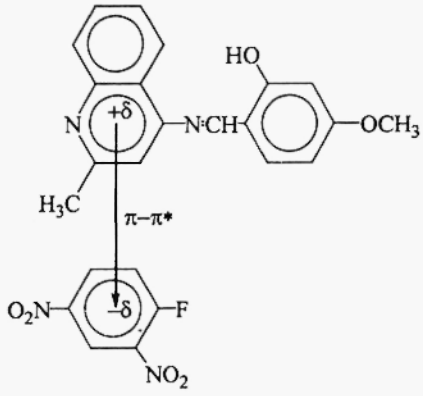
^{1}H NMR Spectra:

Show only signals of the donor being shifted towards lower fields on complex formation with fluoranil and 2,4-dinitrofluoro-benzene, which can be ascribed to the decreased shielding of the protons of the donor ring as a result CT interaction. This can be explained by the greater participation of the

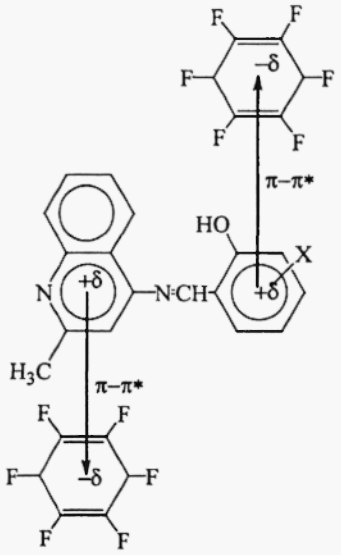
pi-electrons belonging to the corresponding carbon atoms in the HOMO than that by other carbon atom. The spectra of the CT complexes exhibit a broad signal within the 10.5-10.0 ppm range not present in those of the components.



II & DNFB (1:2)



III & DNFB (1:1)



I &FRL (1:2)

This signal with integration equivalent to one proton is assigned to the -OH proton. The signal is broader and lies at higher 5-values and increases in case of 1:2 complexes, this is possible due to the difference in the character of the nitrogen, carrying the positive charge, to which the proton is bonded.

The electronic absorption spectra:

The electronic absorption spectra of the solid molecular complexes in Nujol mull[16] reveal marked shifts of the absorption bands of the donor and acceptors to varied magnitudes to various directions. Besides these shifts, two bands are observed within the 430-550 nm range. The higher energy band at 410-480 nm range would be assigned to the π-π* intermolecular charge transfer interaction, while the second one is due to π-π* charge transfer, the latter involves the transfer of an electron from -NH_2 group to C=O group of the benzoquinone. The energy of the π-π* CT band (E_{CT}) is utilized to estimate the ionization potentials of the donor under investigation using the relation given by Briegleb[(5)].

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

In which I_P is the ionization potential of the donor, EA is the electron affinity of the acceptors fluoranil and 2,4-dinitrofluorobenzene, the C is the coulombic force between the electron transferred and positive hole left behind (5.2 ev)[(5)]. The value of Ip obtained amount 7.68 ev. This is a quite concordant with those determined from the electronic absorption spectra[(17)].

ESR spectra of CT complexes under investigation were obtained at room temperature; the g_{eff} values are given in (Table 2), all CT complexes investigated are ESR-active. The spectra of CT complexes showed an intense sharp signals and their values range between 1.9652-2.9080. The variation in

g_{eff} value for a series of compounds will depend on the orientation of the CT complex with respect to the applied field, and also, any positive contribution to the g-value of single free electron (2.0023) results from the decreased ionic character of the ground state[18].

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