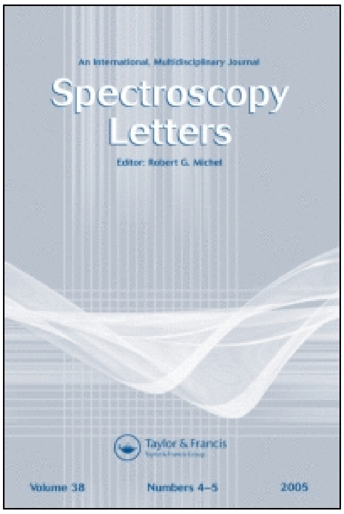

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UV-Visible Spectrophotometric Investigations of Charge Transfer Complexes of Some P-N,N-Dimethylaminobenzylidene Ailines with the New Acceptor PFB and CA Acceptor

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UV-VISIBLE SPECTROPHOTOMETRIC INVESTIGATIONS OF CHARGE TRANSFER COMPLEXES OF SOME P-N,N-DIMETHYLAMINOBENZYLIDENE AILINES WITH THE NEW ACCEPTOR PFB AND CA ACCEPTOR

KEY WORDS: Uv-visible spectrophotometry, charge transfer complex CT, Benesi-Hildebrand equation, Hammett σp,m substituents, benzylidene anilines; 2,3,5,6-tetrachloro-1,4-benzoquinone (chloranil CA); pentafluorobenzaldehyde PFB, extinction coefficient εCT, equilibrium constant K_{CT}, ionization potential Ip, free energy ΔG^o, dissociation energy of the CT complex excited state W, electron affinity Ea, and energy of transition h ν_{CT}.

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ABSTRACT

The CT complexes of PFB and CA acceptors with eleven benzylidene anilines donors have been investigated spectrophotometrically in the uv-visible region for the first time. The values of Ip of these compounds have been estimated from their complexes with CA, the values are in the range of 8.64-8.96 ev. From these values the constants of the new acceptor PFB a, b, C_1,C_2 and Ea have been calculated, the values are 0.91, -5.31, 7.13, 1.97, and 1.37 ev, respectively. The CT parameters of our donors with PFB and CA acceptors, εCT, K_{CT} ΔG^o and W have also been estimated and discussed.

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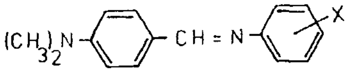

$X = p\text{-}H$,1

$X = p\text{-}N(CH_3)_2$,2

$X = p\text{-}OCH_3$,3

$X = p\text{-}CH_3$,4

$X = p\text{-}NO_2$,5

$X = p\text{-}OH$,6

$X = p\text{-}COOH$,7

$X = p\text{-}Br$,8

$X = p\text{-}Cl$,9

$X = m\text{-}OCH_3$,10

$X = m\text{-}CH_3$,11

Scheme 1

INTRODUCTION

Recently we have studied the CT complexes between iodine acceptor and some Schiff bases donors derived from various aromatic and heterocyclic aldehydes (1,2).

In this work we investigate the CT complexes of the new acceptor PFB and CA acceptor with eleven benzylidene anilines derived from p-N,N-dimethylaminobenzaldehyde and some substituted anilines. The ionization potentials of our donors, the physical constants of the new acceptor PFB and the physical CT parameters , all have been determined and discussed for the first time.

EXPERIMENTAL

All donors (Scheme 1) used throughout this work are well known compounds, were prepared and purified using the procedures described in the literature (3-5). The PFB and CA were of Koch-Light (99% purity) and Fluka (99% purity), respectively. Chloroform was of Fluka spectroscopic grade, all were used directly without further purification. The uv-visible spectra of our donors and of their CT complexes with both acceptors were measured on a Pye-Unicam SP8-400 spectrophotometer using a quartz solution cell of 1.0 cm

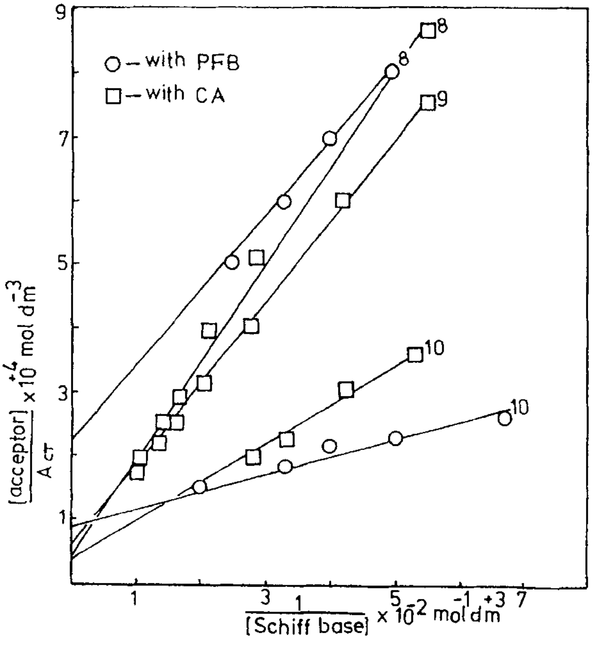

Fig. 1. Benesi-Hildebrand plots of the CT complexes of molecules 8-10 with CA and PFB acceptors. A_{CT} = Absorbance of CT complex at λ_{max}

path length. The reference solution used was $CHCl_3$ containing the same concentration of the donor in every case. The CT complexes were followed by measuring the absorbances of their new absorption bands in the region of 436–484 nm after 24 hours from their preparation at 299 and 300 °K. The concentrations of PFB and CA being kept constant and that of the donor was variable in every set of solutions, the initial concentration of the donor was much greater than that of the acceptor. This was done, because Benesi-Hildebrand equation (equation 1) must be held for 1:1 molecular complexes under these conditions (6,7).

RESULTS AND DISCUSSION

The plots of the initial concentrations of PFB or CA divided by the absorbances of the CT complexes at λ maxs against the reciprocal of the initial concentra-

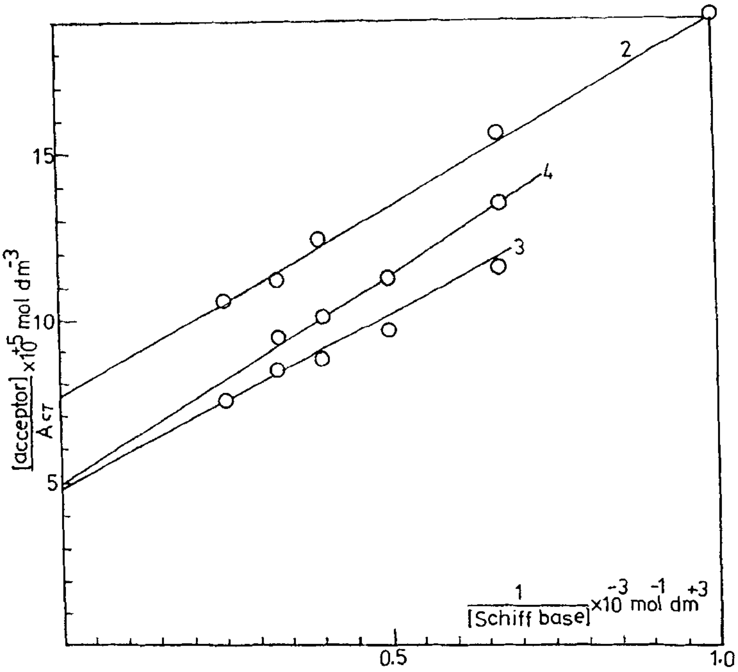

Fig. 2. Benesi-Hildebrand plots of the CT complexes of molecules 2-4 with PF3 acceptor.

Table 1: The Physical Parameters Of CT Complexes Of Molecules 1-11 With CA Acceptor In $CHCl_3$ At 300 K.

No. of molecu.	Donor molecu. λmax(εmax)/ nm(m^2 mol^{-1})	CT complex λmax(εmax)/ nm(m^2 mol^{-1})	h ν_{CT}/ ev	K_{CT}/ mol dm^{-3}	$-\Delta G^0$/ kJ mol^{-1}
1	352 (3280)	436 (4000)	2.84	82 ± 2	10.79
2	380 (2180)	484 (7140)	2.56	1177 ± 10	17.61
3	362 (3330)	442 (2860)	2.80	300 ± 5	14.20
4	354 (4630)	440 (4000)	2.82	176 ± 23	12.88
5[a]	398 (2870)	----------	----	--------	-----
6	358 (2400)	442 (1560)	2.80	640 ± 20	16.09
7[a]	370 (4140)	----------	----	--------	-----
8	360 (3650)	446 (2220)	2.78	30 ± 1	8.47
9	366 (4530)	442 (2220)	2.80	43 ± 3	9.37
10	358 (3340)	440 (2440)	2.82	70 ± 2	10.58
11	354 (3780)	438 (1010)	2.83	165 ± 15	12.72

[a] These compounds do not form CT complexes with CA even at higher concentrations (0.001 mol dm^{-3}).

Table 2: The Physical Parameters Of CT Complexes Of Molecules 1-11 With PFB Acceptor In $CHCl_3$ at 299 K.

No. of molecu.	CT complex $\lambda max(\varepsilon max)$/ nm($m^2$ mol^{-1})	$h\nu_{CT}$/ev	K_{CT}/mol dm^{-3}	$-\Delta G^o$/kJ mol^{-1}
1	437 (1170)	2.84	362 ± 7	14.62
2	482 (1330)	2.57	636 ± 11	16.02
3	442 (2130)	2.80	442 ± 8	15.12
4	436 (2000)	2.84	394 ± 7	14.83
5[a]	---------	----	-------	-----
6	444 (2380)	2.79	430 ± 9	15.05
7[a]	----------	----	-------	-----
8	446 (350)	2.78	216 ± 5	13.34
9	444 (540)	2.79	186 ± 4	12.97
10	440 (1110)	2.82	300 ± 8	14.16
11	436 (800)	2.84	290 ± 6	14.07

[a] These compounds do not form CT complexes with PFB acceptor even at higher concentrations (0.001 mol dm^{-3}).

tions of the donors gave according to Benesi-Hildebrand equation (equation 1) a very good straight lines of which the intercepts equal to ($1/\varepsilon CT$) and slopes equal to ($1/K_{CT}\,\varepsilon CT$).

$$\frac{[\text{acceptor}].l}{A_{CT}} = \frac{1}{K_{CT}\ .\ \varepsilon CT} . \frac{1}{[\text{Schiff base}]} + \frac{1}{\varepsilon CT} \qquad (1)$$

Where A_{CT} is the absorbance at λmax due only to the complex, l is the path length (= 1.0 cm). This equation is valid for 1:1 complex when the initial concentration of the donor is much greater than that of the acceptor. Figures 1 and 2 represent a typical plots of equation 1. From the slopes and intercepts K_{CT} and εCT can be evaluated. Tables 1 and 2 represent the values of $h\nu_{CT}$, εCT, K_{CT} and ΔG^o for CT complexes of CA and PFB with our donors; ΔG^o has

Table 3: The Values Of Ips Of Molecules 1-4, 6 And 8-11, And Ws Of The CT Complexes With CA Acceptor.

No. of molecu.	Ip/ev	W/ev
1	8.96 ± 0.20	4.75
2	8.64 ± 0.22	4.71
3	8.91 ± 0.28	4.74
4	8.93 ± 0.32	4.74
6	8.91 ± 0.28	4.74
8	8.89 ± 0.27	4.74
9	8.91 ± 0.28	4.74
10	8.93 ± 0.32	4.74
11	8.94 ± 0.34	4.74

been calculated from the equation $\Delta G^o = -RT \ln K_{CT}$. The Ip values of our donors, the physical parameters of the new acceptor PFB (a, b, C_1, C_2, and Ea), and W values of CT complexes have been calculated using equations 2-5 (6,7).

$$h\nu_{CT} = aIp + b \tag{2}$$

$$h\nu_{CT} = Ip - C_1 + \frac{C_2}{Ip - C_1} \tag{3}$$

$$W = Ip - Ea - h\nu_{CT} \tag{4}$$

$$Ea_1 = Ea_2 + h\nu_{CT_1} - h\nu_{CT_2} \tag{5}$$

Where a, b, C_1, C_2, and Ea are constants for a particular acceptor; their values for CA acceptor which were used in the calculation of Ip and W values are equal to 0.89, -5.13, 5.70, 0.44, and 1.37 ev, respectively (6); Ea_1 and Ea_2 are the electron affinities of PFB and CA in ev, $h\nu_{CT_1}$ and $h\nu_{CT_2}$ are the energies of transition in ev of their CT complexes with the same donor molecule. The values of Ip and W are represented in Table 3. The PFB constants a, b, C_1, C_2, and Ea have been calculated using equations

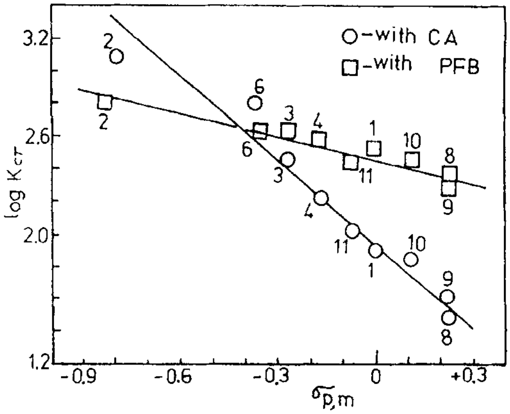

Fig. 3. Correlation of log K_{CT} with Hammett $\sigma_{p,m}$ substituent.

2,3, and 5; the values are 0.91, -5.31, 7.13± 0.14, 1.97± 0.16, and 1.37±0.01 ev, respectively. It seems that the CT complexes of molecules 1-4, 6, and 8-11 with CA and PFB are of the same type, namely $n \longrightarrow \pi^*$, the nitrogen atom of azomethine group ($-\ddot{N}=CH-$) of the donor molecule donates n-electrons to the π^* orbital of the C=O groups of CA and PFB acceptor molecules. This suggestion is based on the followings: (i) the very close values of $h\nu_{CT}$, Ip, and W (Tables 2 and 3); and (ii) the data of Tables 1 and 2 indicate that the formation of CT complex is enhanced when electron donating group is substituted in the para position of the aniline moiety of the donor molecule (Scheme 1), namely molecules 2-4 and 6 compared with molecule 1. These groups increase the electron density of the nitrogen atom of azomethine group, and then enhancing the formation of CT complex; this is confirmed by (a) the linear relationship between $\log K_{CT}$ and Hammett $\sigma_{p,m}$ substituent (Figure 3), and (b) compounds 5 and 7 did not form CT complexes with CA and PFB under our experimental conditions even at higher concentrations, the NO_2 and COOH groups in these compounds decrease the electron density of azomethine group.

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