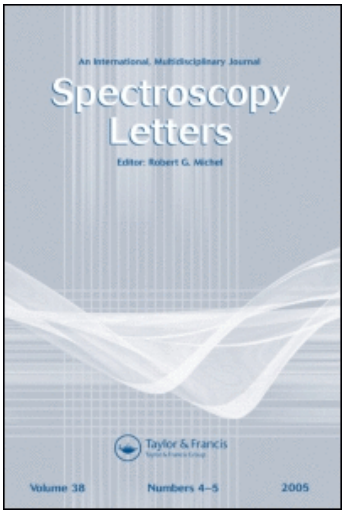

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Spectrophotometric Study on the Charge Transfer Complexes of Iodine Acceptor With Some Schiff Bases n-Donors

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SPECTROPHOTOMETRIC STUDY ON THE CHARGE TRANSFER COMPLEXES OF IODINE ACCEPTOR WITH SOME SCHIFF BASES n-DONORS

KEY WORDS: Uv-visible spectrophotometry, charge transfer CT complex, Bensi-Hildebrand equation, Schiff bases, iodine, extinction coefficient ε_{CT}, equilibrium constant K_{CT}, ionization potential Ip, free energies ΔG°, dissociation eneregies of the charge transfer complex excited state W.

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ABSTRACT

The CT complexes between iodine and fifteen different Schiff bases have been investigated by uv-visible spectrophotometry in chloroform. The equilibrium constants of the CT complexes, the ionization potentials of the Schiff bases, and other physical CT parameters have also been determined and discussed.

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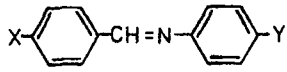
INTRODUCTION

Iodine forms a wide range of CT complexes with amino acids (1-3), purines and pyrimidines (4,5),indoles (6), vitamine B_{12} (7), steroides (8-10), cyclohexane derivatives (11-13), ß-carotene (14-16), retinol (vitamine A gives with aqueous iodine dark blue-green substance)(17, 18), phenothiazine and phenazines (19-21), different amines and pyridines (22-29), some sulfur compounds (30-33), aromatic hydrocarbons (34-36); furans, dioxane, ethers and ketones (37-40); substituted benzamides and acetamides (41,42). On the other hand, molecular CT complex studies of Schiff bases with iodine were very limited. The only studies known are those of benzylidene aniline (43-45), N-benzylamine (44), p-N,N-dimethylaminobenzylidene aniline and benzophenone anil (45).

In the present work the Ip of fifteen Schiff bases; K_{CT}, ε_{CT}, and ΔG° of CT complexes have been calculated from the energies of transition $h\nu_{CT}$ of the CT complex absorption bands for the first time, a study which has not been attempted previously on such Schiff bases with iodine.

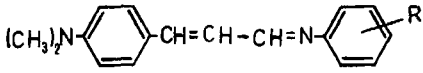
EXPERIMENTAL

All the Schiff bases (Scheme 1) used throughout this work are well known compounds, were prepared and purified using the procedures described in the literature (46-50). Iodine was of Fluka and chloroform was of Fluka spectroscopic grade, they were used directly without further purification. The uv-visible spectra of Schiff bases and of their CT complexes with iodine were measured on a Pye-Unicam SP8-400 spectrophotometer using a quartz solution cell of 1.0 cm path length. The reference solution used was chloroform containing the same concentration of Schiff base in every case. The CT complex was followed by measuring the optical densities of the new absorption bands of



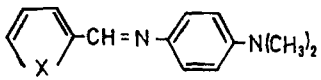
X=H–Y=N(CH$_3$)$_2$,1; X=N(CH$_3$)$_2$–Y=OCH$_3$,2;

X=Y=N(CH$_3$)$_2$,3.

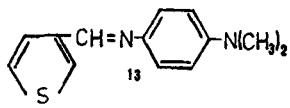


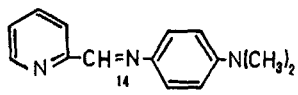
R=p-H,4; R=p-N(CH$_3$)$_2$,5; R=p-CH$_3$,6;

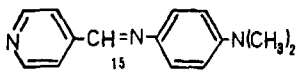
R=p-OCH$_3$,7; R=o-OCH$_3$,8; R=m-OCH$_3$,9.



X=S,10; X=NH,11; X=O,12.







Scheme 1

the complexes in the region of 454 - 562 nm after 24 hours from the preparation at 304 K. The concentration of iodine being kept constant and that of Schiff base was variable in every set of solutions, the initial concentration of Schiff base was greater than that of iodine. This was done, because Bensi - Hildebrand equation must be held for 1:1 molecular complexes under these conditions (51,52). The plot of the initial concentration of iodine divided by the optical density of the complex at λmax against the reciprocal of the initial concentration of the Schiff base gave according to Bensi-Hildebrand

equation (equation 1)a very good straight line of which the intercept equals to ($1/\varepsilon_{CT}$) and the slope equals to ($1/K_{CT}\,\varepsilon_{CT}$), and from these values ε_{CT} and K_{CT} can be

$$\frac{Ao\ l}{A_{CT}} = \frac{1}{\varepsilon_{CT} \cdot K_{CT}} \cdot \frac{1}{Do} + \frac{1}{\varepsilon_{CT}} \qquad (1)$$

evaluated. Ao and Do are the initial concentrations of the iodine acceptor and Schiff base donor respectively; l is the path length (=1.0 cm); A_{CT} is the optical density at λmax due only to the complex, ε_{CT} is the molar extinction coefficient of the complex at λmax, and K_{CT} is the equilibrium constant. This equation is valid for 1:1 complex when $Do \gg Ao$. The concentration of Schiff base was about 5 - 20 times greater than the concentration of iodine.Figures 1 and 2 represent a typical plots of equation 1.

RESULTS and DISCUSSION

Table 1 represents the longer λmax of Schiff bases, $(\lambda max)_{CT}$, $h\nu_{CT}$, ε_{CT}, K_{CT} and ΔG^{o} for CT complexes of iodine with Schiff bases; ΔG^{o} for the complex has been calculated from the values of K_{CT} ($= -RT \ln K_{CT}$). The Ip values of Schiff bases and the values of W of CT complexes have been calculated using equations 2-4 (51,52).

$$h\nu_{CT} = a\,Ip + b \qquad (2)$$

$$h\nu_{CT} = Ip - C_1 + \frac{C_2}{Ip - C_1} \qquad (3)$$

$$W = Ip - Ea - h\nu_{CT} \qquad (4)$$

Where a, b, C_1 and C_2 are constants of iodine, and there values are 0.87, -3.6, 5.2 and 1.5 ev, respectively (51); and Ea is the electron affinity of iodine which is equal to 1.7 ev (40,53). Table 2 represents the average values of Ips and the values of W, the values of Ips which were calculated from equations 2 and 3 agree very well within 96-99.6%.

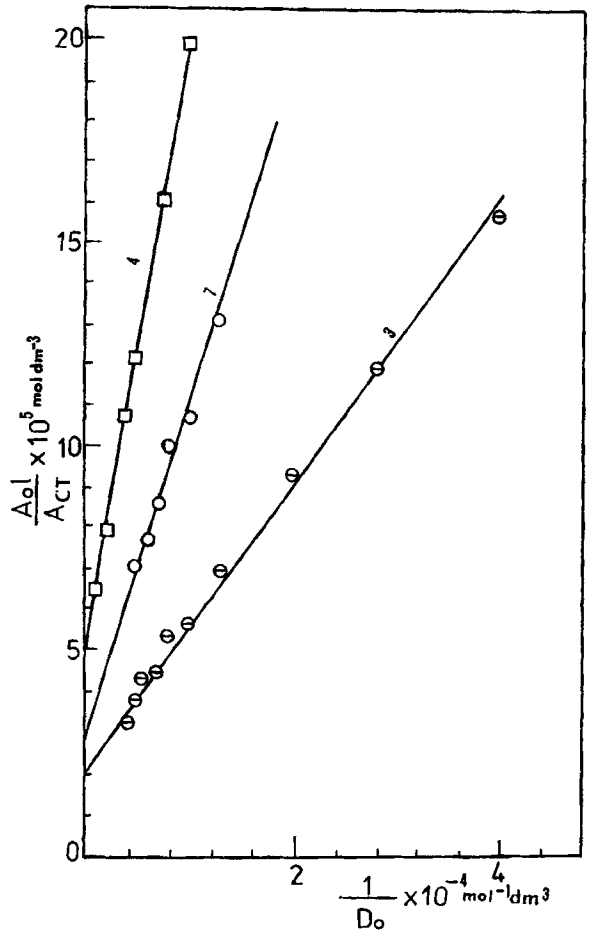


Fig. 1. Bensi - Hildebrand plots of the complexes of molecules 3, 4 and 7 with iodine.

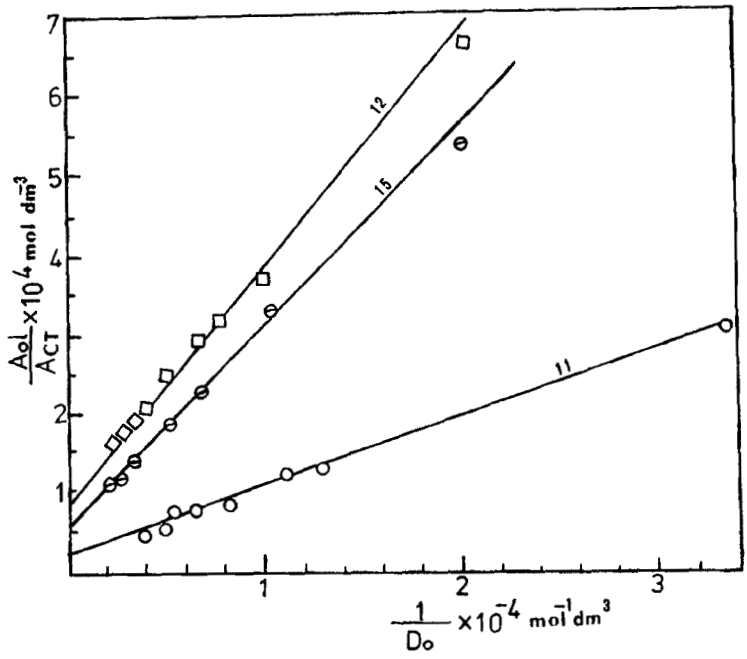


Fig. 2. Bensi - Hildebrand plots of the complexes of molecules 11, 12 and 15 with iodine.

The data of Table 1 indicate that the formation of CT complexes of our Schiff bases with iodine depends largely on the electron density of the nitrogen atom of the azomethine group (-CH=N̈-). This is confirmed by the followings: first, the K_{CT} values of complexes of 1 and 3 are 2.8 and 1.8 times greater than that of 2 respectively, this is because $N(CH_3)_2$ substituent is a strong electron donating group and substituted on the same phenyl ring which contains the nitrogen atom of the azomethine group; on the same basis, the value of K_{CT} of complex 5 is 1.9, 1.7, 3.9 and 3.3 times greater than that of 6, 7, 8 and 9 respectively, the $N(CH_3)_2$ group makes the nitrogen atom of the azomethine a better n-electron donor. Second, the value of K_{CT} of

TABLE 1

Absorption Maxima, Molar Extinction Coefficients, Energies of Transition, Equilibrium Constants and Free Energies of the Complexes of Schiff Bases With Iodine in $CHCl_3$ at 304K.

Schiff Base No.	λ max(ε) Schiff base $nm^{-1}(m^{-2}$ mol)	λ max(ε) Complex $nm^{-1}(m^{-2}$ mol)	$h\nu_{CT}$ ev^{-1}	K_{CT} $mol^{-1}dm^3$	$-\Delta G^o$ $kJ^{-1}mol$
1	380(1690)	496(240)	2.50	8260	22.76
2	360(3300)	454(1600)	2.73	3000	20.20
3	382(2150)	496(5000)	2.50	5500	21.73
4	390(4200)	541(2000)	2.29	3700	20.73
5	382(4310)	562(1100)	2.21	5820	21.87
6	386(4070)	540(2860)	2.29	3050	20.24
7	392(3720)	540(3570)	2.29	3370	20.50
8	388(5640)	544(1180)	2.28	1490	18.44
9	386(3720)	544(1390)	2.28	1770	18.87
10	388(1860)	520(500)	2.38	5000	21.49
11	372(2850)	476(3300)	2.60	3600	20.66
12	386(2150)	520(1180)	2.38	2780	20.01
13	366(1800)	490(1670)	2.53	1600	18.62
14	386(2340)	518(880)	2.39	4105	20.99
15	406(2230)	530(1820)	2.34	2157	19.37

complex 7 is 2.3 and 1.9 times greater than that of 8 and 9 respectively, this is obvious since ortho substituent may hinder donation of n-electrons from nitrogen atom of the azomethine to the iodine molecule. Third, p-N,N-dimethyl-aminocinnamylidene-p-nitroaniline and p-N,N-dimethylamino-benzylidene-p-nitroaniline both did not give CT complexes with iodine at all, in these cases the strong electron withdrawing NO_2 group makes the nitrogen of the azomethine

TABLE 2

The Ionization Potential Values of Schiff Bases and the Dissociation Energies of the CT Excited States W.

Schiff base No.	Ip $(ev)^{-1}$	W $(ev)^{-1}$
1	6.92 ± 0.11	2.71
2	7.14 ± 0.14	3.71
3	6.91 ± 0.11	2.71
4	6.59 ± 0.18	2.91
5	6.53 ± 0.15	2.62
6	6.59 ± 0.18	2.91
7	6.59 ± 0.18	2.91
8	6.58 ± 0.18	2.60
9	6.58 ± 0.18	2.60
10	6.64 ± 0.23	2.56
11	6.99 ± 0.14	2.69
12	6.64 ± 0.23	2.56
13	6.78 ± 0.27	2.55
14	6.65 ± 0.24	2.56
15	7.12 ± 0.28	3.08

a poor n-donor. Fourth ,K_{CT} values correlate well with Hammett σ para and meta substituents for compounds 1-9, Figure 3. On the other hand, the value of K_{CT} of compound 10 is 1.4 and 1.8 times greater than that of 11 and 12. It is well known that the delocalization of the oxygen lone pair of electron with the four π-electrons of butadiene system of the furan ring is lowest, because of the higher nuclear charge of oxygen compared with nitrogen (48). The sulfur atom has approximately the same electronegativity of carbon, hence conjugation of the sulfur electrons with the four π -

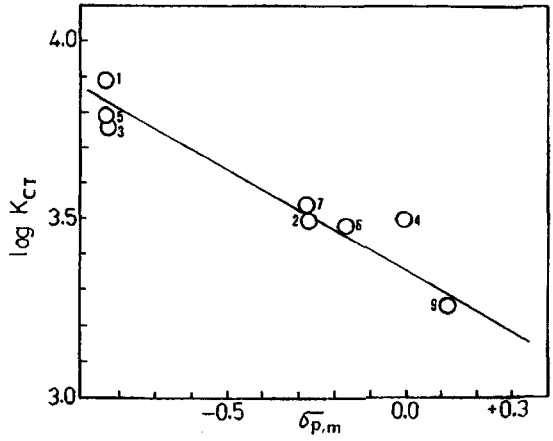


Fig. 3. Plot of log K_{CT} of CT complexes of compounds 1-7 and 9 with Hammett $\sigma_{p,m}$ substituents.

electrons is more complete than in oxygen or nitrogen analog, thus making the thiophene ring a better electron donor which in turn increases the electron density of the nitrogen atom of the azomethine group. The value of K_{CT} of compound 10 is 3.1 times greater than that of 13, and the value of K_{CT} of 14 is 1.9 times greater than that of 15, apparently the effect of substituent in the 2-position is greater than the effect of the same substituent in the 3- or 4-position.

Accordingly, we can conclude that the CT complexes between iodine and our Schiff bases are of $n \rightarrow \sigma^*$ type, in which the interaction is between iodine molecule and the lone pair of electron of the nitrogen atom of the azomethine group, this is confirmed by: (i) the close values of W (Table 2) which indicates that all complexes have the same nature of chemical interaction, and (ii) the low values of ionization potentials of our heterocyclic Schiff bases, compounds 10-15 (Table 2), compared

with the ionization potentials values of 8.87, 8.20, 8.90 and 10.20 ev for the unsubstituted thiophene, pyrrole, furan and pyridine rings, respectively (54,55), this indicates that the donor group is the azomethine.

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