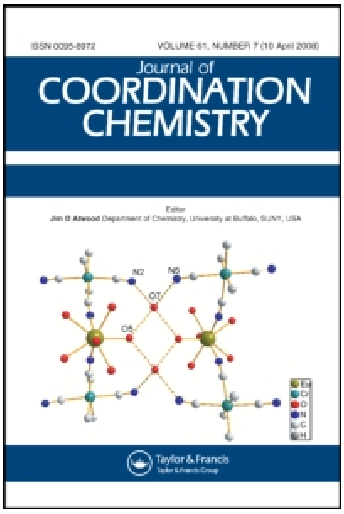

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Electronic Spectroscopic Studies of the Charge Transfer Complex of N , N , N ', N '-Tetramethyl-4-4'-Diamino-Benzophenone with Iodine in Methanol

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ELECTRONIC SPECTROSCOPIC STUDIES OF THE CHARGE TRANSFER COMPLEX OF *N,N,N′,N′*-TETRAMETHYL-4-4′-DIAMINO-BENZOPHENONE WITH IODINE IN METHANOL

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The UV-visible absorption bands of the charge transfer (CT) complex of *N,N,N′,N′*-tetramethyl-4,4′-diaminobenzophenone with iodine in methanol at 30°C have been studied. The value of K^{AD}, ε^{AD} and E_{CT} were calculated for this complex. The value of the equilibrium constant, K^{AD}, for the above complex reaction was calculated as $28.85\,m^3 \cdot mol^{-1}$. The value of the molar extinction coefficient of the CT complex, ε^{AD}, was also calculated as $1171\,m^2 \cdot mol^{-1}$ for $\lambda_{max} = 602\,nm$ and the absorption band energy E_{CT} of the complex was found to be 2.06 e.v.

The ionization potential of the electron donor was also obtained spectroscopically and found to be 6.284 e.v. The rate constant obtained for the forward reaction is $3.624 \times 10^{-5}\,M^{1/2}\,s^{-1}$ and for the reverse reaction is $1.256 \times 10^{-6}\,s^{-1}$.

Finally, the half-life value for the above reaction was graphically calculated and shown to be 1.549 day.

The kinetics of the above reaction were studied showing the reaction to be a half-order reaction. The values of rate constants and half-life were calculated.

Keywords: Iodine; Benzophenone; Electronic spectroscopy; Charge transfer

INTRODUCTION

Comprehensive UV-visible spectroscopic studies on CT complexes of nitrogen compounds were done in different solvents using acceptors such as iodine, bromine, picric acid, trichloro- and trifluoro-acetic acid [1–4]. The equilibrium constant (K^{AD}) and molar extinction coefficients (ε^{AD}) can be calculated by using the Benesi–Hildebrand equation [5]:

$$\frac{[A_0]}{A} = \frac{1}{K^{AD}\varepsilon^{AD}[D_0]} + \frac{1}{\varepsilon^{AD}} \tag{1}$$

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where, A is absorbance of the CT band at λ_{max}, $[A_0]$ is initial concentration of the acceptor, $[D_0]$ is initial concentration of the donor, K^{AD} is equilibrium constant of the CT complex's reaction in solution and ε^{AD} is molar extinction coefficient of the CT complex.

The CT complexes can also be studied by evaluating their electronic absorption band energies. The ionization potentials of electron donors can be obtained from CT absorption bands using different approaches as in the following equations [6–9]:

$$h\,\nu_{CT} = I^D - C_1 + \frac{C_2}{I^D - C_1} \tag{2}$$

$$h\,\nu_{CT} = aI^D + b \tag{3}$$

$$I^D = 4.39 + 0.857\ h\nu_{CT} \tag{4}$$

$$I^D = 5.1 + 0.7\,h\,\nu_{CT} \tag{5}$$

where, $h\nu_{CT}$ is absorption band energy of the CT complex in e.v., I^D is ionization potential of the electron donor in e.v., C_1, C_2, a and b in Eqs. 2 and 3 are constants and their values for the iodine acceptor in CCl_4 are as follows [6–9]: $C_1 = 5.2$ e.v., $C_2 = 1.5$ e.v., $a = 0.67$ or 0.87, $b = -1.9$ or -3.6.

The values of $h\nu_{CT}$ and I^D can be calculated from Eqs. 2–5. The kinetics of the association of electron donors with electron acceptors have been studied [10,11]. In this work, we have studies the behavior of the *N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-benzophenone with iodine in methanol using electron absorption spectroscopy and kinetic studies of their equilibrium in methanol at 30°C.

EXPERIMENTAL

N,*N*,*N*′,*N*′-Tetramethyl-4,4′-diamino-benzophenone (Fluka) with a purity of (98–99.9%) and methanol with purity of (99.5%) from Riedel DeHaen were used directly. The UV-visible spectra were measured using a Pye Unicam SP8-100 spectrophotometer and quartz cells of 1.0 cm path length. The complex was prepared by mixing variable amounts of donor solution to a constant volume of the acceptor solution in methanol. The donor concentrations ranged between 1×10^{-4} and 9×10^{-4} M while the acceptor concentration remained constant (1×10^{-4} M).

RESULTS AND DISCUSSION

The location of the absorption bands of the donor, the acceptor and their complex as well as their molar extinction coefficients are given in Table I. The CT bands of the complex are 209, 260, 572 and 602 nm. The donor bands in methanol are 205, 245 and 365 nm, while those for iodine in methanol are 225, 288, 360 and 455 nm.

All absorption bands of the CT complex are different from those of the donor and acceptor. The clearest ones are at 572 and 602 nm in the visible region. This red

TABLE I Absorption maximum, molar extinction coefficients, equilibrium constant and energy of CT complex of the donor *N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-benzophenone with iodine in methanol at 30°C

Donor		*Acceptor* (I_2)		*Complex*			
λ (nm)	ε ($m^2 mole^{-1}$)	λ (nm)	ε ($m^2 mole^{-1}$)	λ (nm)	ε^{AD} ($m^2 mole^{-1}$)	K^{AD} ($m^3 mole^{-1}$)	E_{CT} (e.v.)
205	10360	225	11450	209	–	–	–
245	9773	288	3645	260	–	–	–
365	1550	360	1495	572	–	–	–
–	–	445	1429	602	1171	28.85	2.060

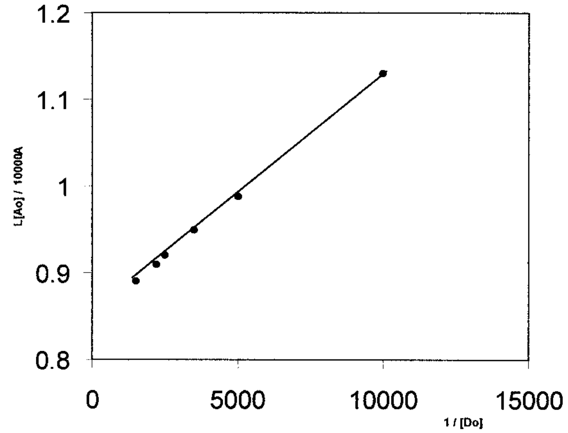

FIGURE 1 Plot of Benesi–Hildebrand Eq. (5).

TABLE II Calculated values of the ionization potential of the donor with iodine acceptor in methanol at 30°C

Equation	I^D (e.v.)
2	6.230
3	6.208
4	6.155
5	6.542
Average value	6.284

shift in the absorption bands of the complex is probably due to the polarization of methanol by the transition dipole [12]. The extent of the shift is related to the refractive index of the solvent. This red shift occurs when a non-polar donor molecule is used in a polar solvent [12].

The values of ε^{AD} and K^{AD} were calculated using the Benesi–Hildebrand equation [5], plotted in Fig. 1, the values obtained are shown in Table I, which also gives the value of the energy of the CT complex, 2.060 e.v. for the 602 nm absorption band. Table II, shows the values of the ionization potential of the donor molecule in methanol with iodine acceptor using Eqs. 2, 3, 4 and 5; these values range between 6.155 and 6.542 e.v. with an average of 6.284.

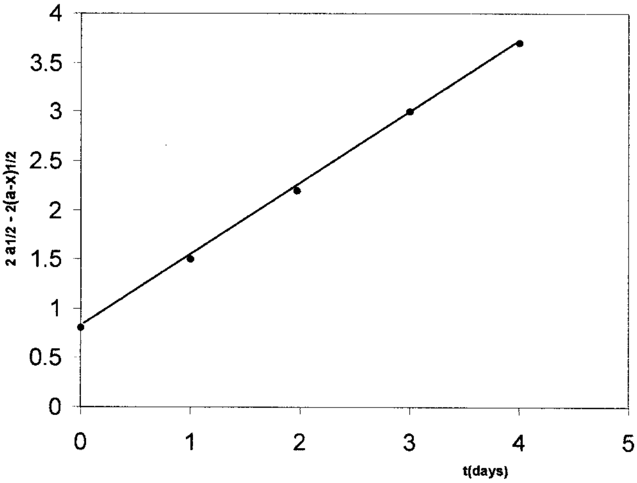

FIGURE 2 Plot of Eq. (6).

The reaction of the donor *N*,*N*,*N*′,*N*′-tetramethyl-4,4′-diamino-benzophenone with iodine in methanol at 30°C is shown to be a half-order reaction as in Fig. 2 using the following equation [13]:

$$kt = 2a^{1/2} - 2(a-x)^{1/2} \tag{6}$$

When using the following equation:

$$k_{-1} = k_1(a - x_e)/x_e \tag{7}$$

where, x_e is the concentration of the reaction product at equilibrium, the rate constant of the forward reaction was calculated as $3.624 \times 10^{-5}\,\mathrm{M}^{1/2}\,\mathrm{s}^{-1}$ and that for the reverse reaction is $1.256 \times 10^{-6}\,\mathrm{s}^{-1}$ [13].

The half-life of the above reaction (t ½) is found to be 1.338×10^{-5} s (or 1.549 day).

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