



Spectroscopic Studies on Charge-Transfer Complexation of Iodine with Two Recently Synthesized Ligands in Chloroform Solution

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ABSTRACT

The interaction of two recently synthesized ligands, a: 5-(2-hydroxybenzylidene)-1,3-dimethylpyrimidine-2,4,6 (1H,3H,5H) - train and b: 5-(2-hydroxy-5-nitrobenzylidene)-1,3-dimethylpyrimidine-2,4,6 (1H,3H,5H)- train with π acceptor (iodine) have been studied spectrophotometrically in chloroform solution. The formation constants (K_f) of complexes were established by using a Benesi-Hildebrand equation and mole ratio data. Formation of the CT complexes with iodine was confirmed by NMR and IR spectroscopies.

Keywords: Iodine; Benesi hildebrand equation; Formation constant; Charge transfer complex

INTRODUCTION

Considerable attention has been directed to artificial receptors for biologically active molecules. Since the most suitable compounds for this purpose are the derivatives of barbituric acid, which are members of the pyrimidine family. However, their biological activity is mainly attributed to tautomeric, acid-base equilibrium and to the nature of the substituents [1]. Moreover, compounds containing pyrimidine ring play an important role in many biological systems, where they exist in nucleic acids, several vitamins, coenzymes and antibiotics [2]. Metal complexes of pyrimidines as well have a great variety of biological activities such as antimalarial, antibacterial, antitumor and antiviral activities [3-7]. Well known pyrimidines are barbituric acid derivatives that constitute a class of drugs that have diverse applications such as sedatives, hypnotics and anticonvulsants and are also employed for anesthesia [8,9]. They are also used for the treatment of anxiety, epilepsy and other psychiatric disorders and possess effects on the motor and sensory functions [10,11]. Barbituric acid derivatives also exert important action on the central nervous system (CNS) [12]. Electron donor-acceptor (EDA) or charge transfer complexes (CT) are recently gaining importance as potential high efficiency nonlinear optical materials, organic superconductors as well as photocatalysts. EDA interaction is also important in the field of drug-receptor binding mechanism, in solar energy storage and surface chemistry as well as many biological fields [13]. Condensation of barbituric acid with Benzaldehyde yielded (L_1 and L_2) which were characterized using IR and ^1H NMR spectra (Figure 1).

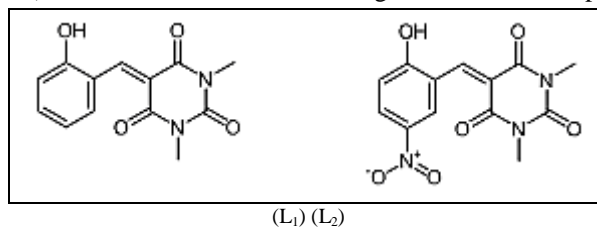


Figure 1: Condensation of barbituric acid with Benzaldehyde yielded (L_1 and L_2)

EXPERIMENTAL SECTION

Instruments

All UV-Vis, spectra were recorded with a WPA- Biowave spectrophotometer using a 10 mm quartz cell. IR spectra of the ligand compound as KBr pellet were recorded using a Nexus 670 spectrometer ($400\text{-}4000\text{ cm}^{-1}$). The $^1\text{H-NMR}$ spectra were recorded on a broker FT-NMR spectrometer (300MHZ). In all experiments, TMS was used as an internal standard.

Reagents

Recently synthesized ligands are of the highest purity available and used without any further purification except for vacuum drying. Chloroform (Aldrich) was of the highest purity and used without any further purification except vacuum drying.

Procedure

Two series of solutions, containing $6.9 \times 10^{-4}\text{ M}$ iodine in chloroform solution in the presence of an increasing amounts of (L_1 , L_2) was prepared and allowed to reach equilibrium. Then, the electronic absorption spectra of the solutions were recorded at $25.0 (\pm 0.1)^\circ\text{C}$.

RESULTS AND DISCUSSION

The molecular interactions between electron donors and acceptors are associated with the formation of colored charge transfer complexes, absorbing radiation in the visible region of the spectrum. In order to study the complex formation reaction of Ligands with I_2 , solutions containing $6.9 \times 10^{-4}\text{ M}$ I_2 in chloroform, in the presence of an increasing amounts of ligands (L_1 , L_2) were prepared and allowed to reach equilibrium. The stoichiometry of the CT complex formed, in all the cases, was determined by applying the mole ratio method using absorption spectral data. The absorption spectrum of I_2 and $L\text{-I}_2$ in chloroform solution and mole ratio plots is shown in (Figures 2-5).

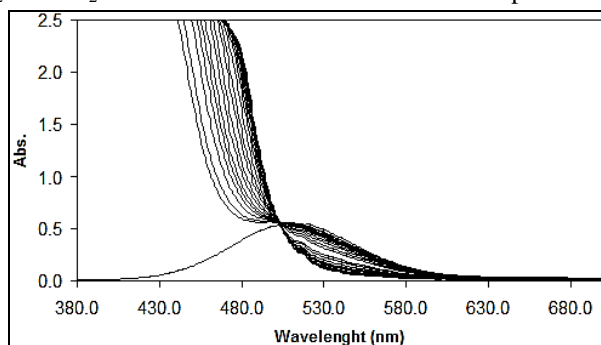


Figure 2: Electronic absorption spectra of iodine in the presence of increasing concentration of L_1 at 25°C . The L_1/I_2 mole ratios are: 0, 3.02, 3.78, 5.29, 6.81, 8.32, 9.84, 12.86, 15.89, 21.95, 28.11, 46.92, 65.85, 84.77, 103.69, 122.62, 141.59, 160.46, 179.39, 198.38, 217.23

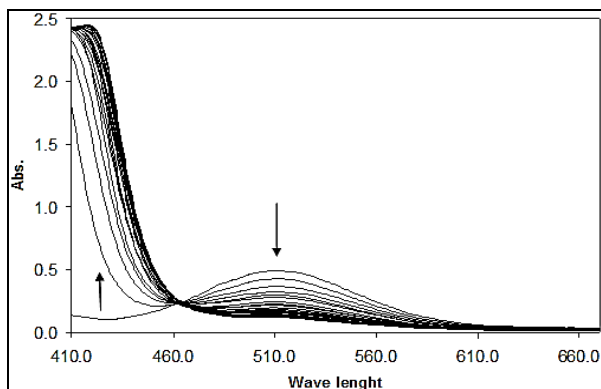


Figure 3: Electronic absorption spectra of iodine in the presence of increasing concentration of L_2 at 25°C . The L_2/I_2 mole ratios are: 0, 2.10, 4.21, 6.32, 8.43, 10.54, 12.65, 14.76, 16.86, 18.97, 21.08, 23.19, 25.30, 27.41, 29.52, 31.63, 33.73, 35.87, 37.95, 40.06, 42.17, 44.28, 46.39

It is well known that, in the resulting 1:1 complexation process, donating of electron density from non-bonding HOMO orbitals of the donor molecule in to the σ^* antibonding LOMO orbital of I_2 , lying along its main axis, decreases the bond order and, consequently, leads to an increase in the I-I bond distance. The higher the strength of the donor- acceptor interaction, the greater the amount of charge transferred from the non- bonding orbital of the donor to the σ^* antibonding of I_2 , and the larger the increases in the I_2 bond distance. Practically, the formation of the resulting charge transfer adduct can easily be noticed in solution by the observation of a new strong absorption band in the UV-Vis spectra of the donor- acceptor mixtures, which can be used to evaluate the equilibrium constant of the $D+ I_2=DI_2$ reaction. Thus, the formation constants of the resulting 1:1 L: I_2 complexes were determined by the observed measurements at 517 nm for L_1 and 512 nm for L_2 with varying excess concentration of L_1 , L_2 and constant iodine concentration (6.9×10^{-4} M) in chloroform. Since both the donor and acceptor concentrations are very low and comparable, the following modification of the Benesi- Hildebrand equation was used [14]. Formation constants of the resulting 1:1 donor-acceptor complexes were determined employing the blue-shifted iodine bands for a series of solutions with varying excess amounts of the ligand and constant iodine concentration in all three solvent systems used. The formation constants, K_f , and molar absorptivity, ϵ_{CT} , of the complex were evaluated using Benesi-Hildebrand equation (1):

$$[I_2]_o / Abs = (1/K_f \epsilon_{CT})(1/[L]_o) + 1/\epsilon_{CT} \quad (1)$$

Where $[I_2]_o$ and $[Donor]_o$ are the initial concentrations of reactants. Sample linear plots of $[I_2]_o / Abs$ vs. $1/[Donor]_o$ are shown in Figures 6 and 7, from the intercept and slope of which the ϵ_{CT} and K_f values can be evaluated. Such a fair linear relationship in the resulting Benesi-Hildebrand plots is a good evidence for the 1:1 stoichiometry of the charge transfer complexes studied [15] (Table 1).

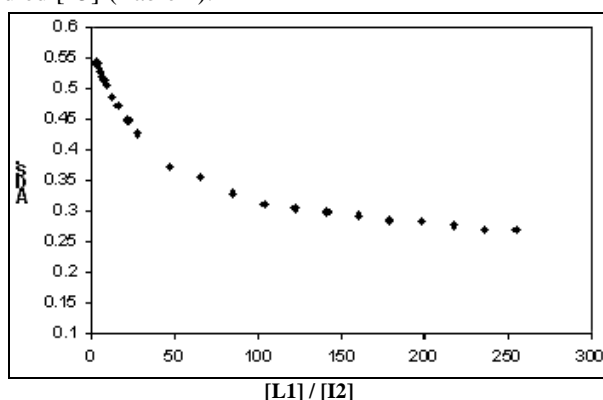


Figure 4: The mole ratio plot for L1- I_2 in chloroform solution at 517 nm at 25°C

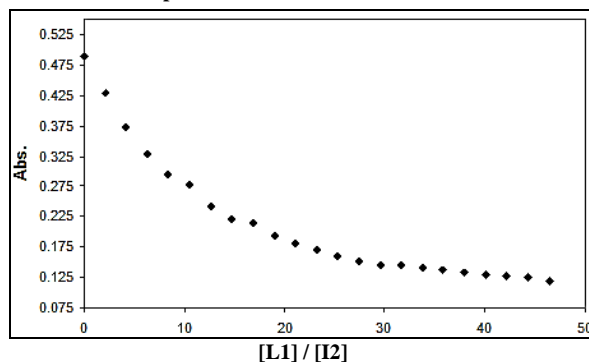


Figure 5: The mole ratio plot for L2- I_2 in chloroform solution at 512 nm at 25°C

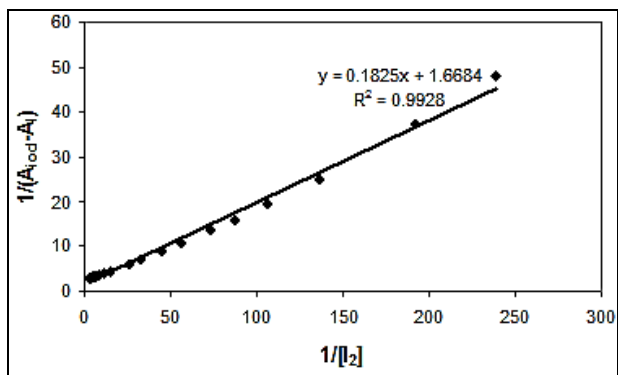


Figure 6: Benesi- Hildebrand plot for L1- I2 complex in chloroform solution at 25°C

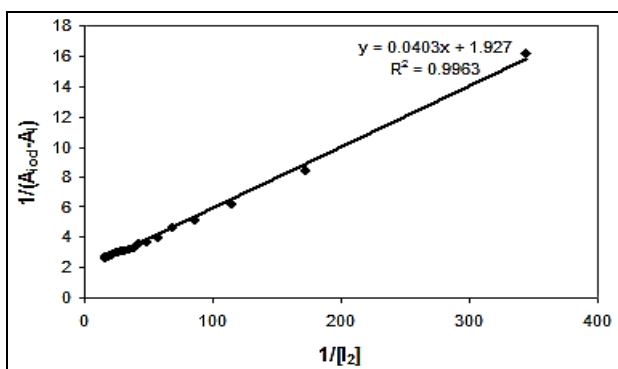


Figure 7: Benesi- Hildebrand plot for L2- I2 complex in chloroform solution at 25°C

Table 1: The resulted Kf values are gathered

Complex	Stoichiometry	Formation constant(k_f)
L ₁ - I ₂	ML	9.141
L ₂ - I ₂	ML	47.81

CONCLUSION

Based on the results; the two ligands can participate in the complex formation reaction, but comparison between two ligands revealed that L₂ complexes are stronger than L₁ in chloroform solution due to the added NO₂ group. It is clearly shown that the formation of charge transfer complexes is via this NO₂ group. This conclusion is confirmed by HNMR and IR studies too, the spectra not included here.

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