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Spectrophotometric Studies of the Charge Transfer Complexes formed between Pyridine and its Amino Derivatives (Donor) and DMAD (Acceptor)

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Abstract : Nitrogen-containing heterocyclic compounds are of special interest as they behave as n- as well as π electron donors. Charge-transfer complexes of Pyridine and its amino derivatives are widely used by the pharmaceutical, textile, agricultural and other industries. Keeping in view, in the present work, formation of charge transfer complexes between the pyridine & its amino derivatives (donor) and DMAD (acceptor) have been investigated. The stoichiometry of the synthesized CT complexes was determined by mole ratio method spectrophotometrically and found to be 1:1.The formation constant and molar extinction coefficient of each synthesized charge transfer complex was also determined using Benesi-Hildebrand equation.

Keywords : Charge transfer Complexes, Pyridine, Picoline, Mole-ratio method, Benesi-Hildebrand equation.

Introduction

Charge transfer complexes using organic species are intensively studied because of their special type of interaction, which is accompanied by transfer of an electron from the donor to the acceptor[1].When solutionof two reagents (donor and acceptor) are mixed, the marked change in colour clearly indicates the formation of complex[2]. The principal feature of complex formation is the appearance of a new and intense absorption band in the ultra-violet or visible region and this is due to an electronic transition into an excited electronic forces. The excitation energy of this transition occurs in the visible region of the electro-magnetic spectrum, which produces the intense colour[3].

Charge transfer complexes are present in many synthetic and natural materials ranging from carbon black to metallo-proteins. The presence of charge transfer complexes in polymers and the interaction of oxygen and metals with radiation absorbing materials have far ranging consequences in applications that require environmental stability in space and aerospace applications. Charge transfer complex studies brought development in the field of chromatography, carbonless imaging and estimation of solvent polarity, ionization potential, electron affinity. Recently charge transfer complexes are gaining importance as potential high efficiency non-linear optical materials. Such complexes have been and are recently being reported to act as reaction intermediate[4]. CT complexes are also being regarded as important materials for use as organic superconductors, photo catalysts and dendrimers. They are also finding application in solar energy storage, mechanism of drug action, non-linear optical activity, surface chemistry and molecular recognition[5]. Charge transfer complex is an important phenomenon in biochemical and bioelectrochemical energy transfer

processes[6-7].Some of the CT complexes are also reported to be electro-conducting. Good CTC conductors are formed between good donor and acceptor pairs whose molecular shapes are flat[8].

Nitrogen-containing heterocyclic compounds are of special interest as they behave as n- as well as π electron donors[9]. The formation of charge transfer complexes of nitrogen heterocyclic compounds with iodine is known to involve the non-bonding electrons on the nitrogen atoms[10]. Charge-transfer complexes of Pyridine and its derivatives are widely used by the pharmaceutical, textile, agricultural and other industries. In the agricultural sector, these compounds are used to exterminate weeds, fungi, insects, and other parasitic plants. In the pharmaceutical industry, they are widely used as a material for making anti-allergic and ant tubercular drugs, antiseptic, analgesic, and in a treatment of vitamin B6 complex deficiency. In the textile industry, they are reported to be used as a water-proofing material for making water-proof textile[11]. Methyl substituted pyridine derivatives (picolines) have many pharmaceutical and biological applications, they have intense hypolipidemic effect, antineoplastic and anti-inflammatory activities. They have good activity against leukemia and human glioma cell growth[12].Aminopicolines also constitute an important group of electron donors or proton acceptors, and they have various medical and pharmacological applications, especially 2-amino-4-picoline. It is used as an intermediate for many pharmaceutical applications, and it is also used as a potent inhibitor for inducible NO synthase activity in vitro and in vivo[13].

A number of reports have been found pertaining to the formation of charge transfer complexes of amino and halogen substituted pyridine with suitable acceptors i.e. chloranil, malic-anhydride, α-nitroso-β-naphthol etc[14-26]. A very few reports have been found involving the formation of charge transfer complexes of picolines (methyl pyridines). Soit was thought worthwhile to synthesize CT complexes of amino picolineswith suitable π-acceptor (DMAD). The absorption maxima of these complexes was determined spectrophotometrically. The stoichiometry of the complexes was also determined using mole-ratio method. Benesi-Hildebrand equation was used to determined the formation constants.

Experimental Details

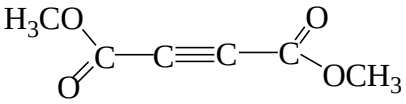
Materials and Equipments

All reagents and solvents were obtained from commercial suppliers and were used without further purification. The electronic absorption spectra of donors and acceptor were recorded using a Shimadzu 160 UV-vis spectrophotometer in the 200-700 nm region with a quartz cell of 1.0 cm path length.

Methodology : Prepration of the stock solutions

Acceptor

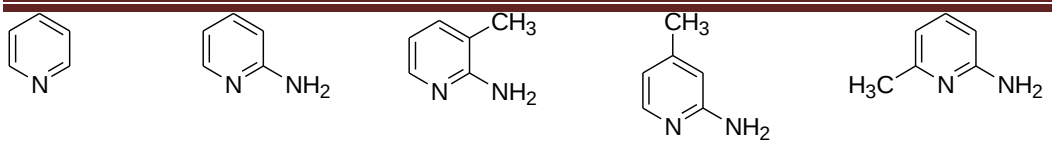
A solution of Dimethylacetylenedicarboxylate **(**DMAD acceptor) of a concentration of 0.1M in 25ml was prepared in volumetric flask by dissolving 0.30 ml of it in DMSO.



DMAD

Donor

A solution of donor (pyridine and its amino derivatives) of a concentration of 0.1M in 25 ml was prepared in volumetric flask by dissolving pyridine **(a)** (0.20 ml), 2-amino pyridine **(b)** (0.24 gm), 2-amino-3-picoline **(c)** (0.25 ml), 2-amino-4-picoline **(d)** (1.08 gm), 2-amino-6-picoline **(e)** (0.25 ml) in dimethyl sulphoxide (DMSO).



a **b** **c** **d** **e**

The electronic absorption spectra were recorded individually for acceptor and each donor spectrophotometrically in the 200-400 nm region and presented in Table 1.

Table 1: Absorption maxima (nm) of different donors and acceptor in DMSO

	DMAD	**Pyridine (a)**	**2-Amino pyridine (b)**	**2-Amino-3-picoline (c)**	**2-Amino-4-picoline (d)**	**2-Amino-6-picoline (e)**
λ_{max}(nm)	330	310	310	340	340	330

Table2: Solutions analyzed

Sample Solutions	**Ia-e**	**IIa-e**	**IIIa-e**	**IVa-e**	**Va-e**	**VIa-e**	**VIIa-e**	**VIIIa-e**
DMAD solution (Acceptor) ml	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Conc. of DMAD (mol/L)	10^{-1}	10^{-1}	10^{-1}	10^{-1}	10^{-1}	10^{-1}	10^{-1}	10^{-1}
Donor solution mL	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Conc. of donor (mol/L)	0.5×10^{-1}	1.0×10^{-1}	1.5×10^{-1}	2.0×10^{-1}	2.5×10^{-1}	3.0×10^{-1}	3.5×10^{-1}	4.0×10^{-1}
DMSO (mL)	8.5	8.0	7.5	7.0	6.5	6.0	5.5	5.0

Table 3: Absorbance of different CT-complexes (CTa-e) having 1:1 mole ratio

Wave length(nm)	**CT_a**	**CT_b**	**CT_c**	**CT_d**	**CT_e**
350	2.986	3.944	3.922	3.884	3.877
360	2.722	3.939	3.915	4.000	3.957
370	2.689	3.706	3.944	3.830	3.465
380	2.977	3.981	3.507	3.962	3.638
390	3.050	3.971	3.523	3.973	3.533
400	3.083	3.954	3.515	3.821	3.231
410	3.135	3.985	3.671	3.950	3.085
420	3.078	4.000	3.498	3.944	2.910
430	3.084	3.945	3.533	3.916	2.776
440	2.981	4.000	3.471	3.923	2.648
450	2.709	3.996	3.411	3.746	2.581
460	2.331	4.000	3.468	3.656	2.520
470	1.888	4.000	3.544	3.670	2.472
480	1.469	4.000	3.694	3.636	2.443
490	1.066	4.000	3.784	3.654	2.415

500	0.731	4.000	3.865	3.558	2.340
510	0.486	4.000	3.643	3.303	2.167
520	0.338	3.958	3.140	2.687	1.806
530	0.242	3.074	2.340	1.899	1.320
540	0.178	1.991	1.528	1.194	0.880
550	0.142	1.253	0.954	0.723	0.522
560	0.118	0.778	0.591	0.481	0.295
570	0.099	0.463	0.381	0.327	0.173

Determination of stoichiometry of the above synthesized CT complexes (CTa-e)

Spectrophotometric titration measurements were performed to determine the stoichiometries of the formed CT-complexes. A series of the solutions [**I(a-e)** to **VIII(a-e)**] for each donor-acceptor system was prepared in such a way that the donor concentration varied from 0.5 to 4.0×10^{-1} mol/L, while concentration of the acceptor (DMAD) remained constant, i.e. 10^{-1} mol/L (Table 2). Different aliquots of the stock solutions of pyridines and its amino derivatives containing 0.5 to 4.0 mL were transferred into boiling-tubes. To each boiling-tube, 1 mL of stock solution of DMAD was added. The reaction mixture was completed to 10 mL with the same solvent. A light red to red color was obtained immediately after the mixing of donor and acceptor. The absorbance was measured against a blank at the corresponding wavelengths of maximum absorbance ($\lambda_{max(CT)}$) of the complex. From the determination of the conventional spectrophotometric molar ratio, the stoichiometry of the CT-complexes **(CTa-e)** was obtained using a plot of the absorbance of each CT-complex as a function of the conc.(donor):conc.(acceptor) ratio.

Table 4: Absorbance of the CT complexes (CTa-e) in DMSO at room temperature

Sample solution	C_d/C_a	CTa (λmax=500nm)	CTb (λmax =550)	CTc (λmax =500)	CTd (λmax =520)	CTe (λmax =520)
I	0.5	1.063	1.115	3.031	2.430	1.806
II	1.0	1.731	1.253	4.000	3.558	1.927
III	1.5	0.825	1.409	3.998	4.000	1.527
IV	2.0	0.912	1.724	4.000	4.000	1.699
V	2.5	0.860	1.863	4.000	4.000	1.821
VI	3.0	0.916	1.391	4.000	4.000	1.683
VII	3.5	1.009	1.529	4.000	4.000	1.243
VIII	4.0	1.526	1.510	4.000	4.000	1.362

Determination of formation constant (K_{CT}) and molar extinction (ε_{CT}) of the above synthesized CT complexes (CTa-e)

The spectrophotometric data so obtained (Table-4) were used to calculate values of the equilibrium constant (K_{CT}) and the molar extinction coefficients, ε_{CT} of the CT-complexes in DMSO for **CTa-e** having stoichiometries using the modified Benesi-Hildebrand equation [27].

$$\frac{C^{\circ}_d . C^{\circ}_a}{A} = \frac{1}{\mathcal{E}K_{CT}} + \frac{C^{\circ}_d + C^{\circ}_a}{\mathcal{E}}$$

Where C^0_d and C^0_a are the initial concentration of the electron-donor and electron-acceptor, respectively and A is the absorbance of the CT band.

Results and Discussion

The electronic absorption spectra of acceptor (DMAD) and donors (pyridine and its amino derivatives **a-e**) were recorded individually, and observed below 340 nm, shown in Table-1**,** as the solution prepared in both the cases were observed cream to light yellow in color.

Light red to dark red colour developed on mixing the solution of donors (**a-e)** with the colourless solution of DMAD in DMSO. Appearance of red colour indicated formation of the CT-complexes (**CTa-e**). Scanning of the complexes, **IIa-e** (Table 2) in the UV-visible region between 200-700 nm gave λ_{max} peaks at 500, 550, 500, 520, 520 nm respectively and the electronic absorption spectra of 1:1 CT- complexes (**CTa-e**) in DMSO are shown in Table 3 and presented in Fig. 1.

The stoichiometry of the synthesized CT-complexes **CTa-e** were determined using methodology discussed in experimental section and a graph (Fig. 2) plotted against the absorbance of each CT complexes and ratio of conc. of donor conc. of acceptor. The values are presented in Table 4.

It is seen from the Fig. 2 that absorbance of all the CT-complexes increases with increasing the concentration of donor but after 1:1 stoichiometry, it becomes nearly constant, which predicts 1:1 stoichiometry of the CT-complexes formed between the donor (pyridine and it's amino derivatives) and DMAD.

Electronic absorption spectra of different charge-transfer complexes **(CTa-e)** in DMSO at room temperature against their absorption maxima are presented in Fig. 3-7**.**

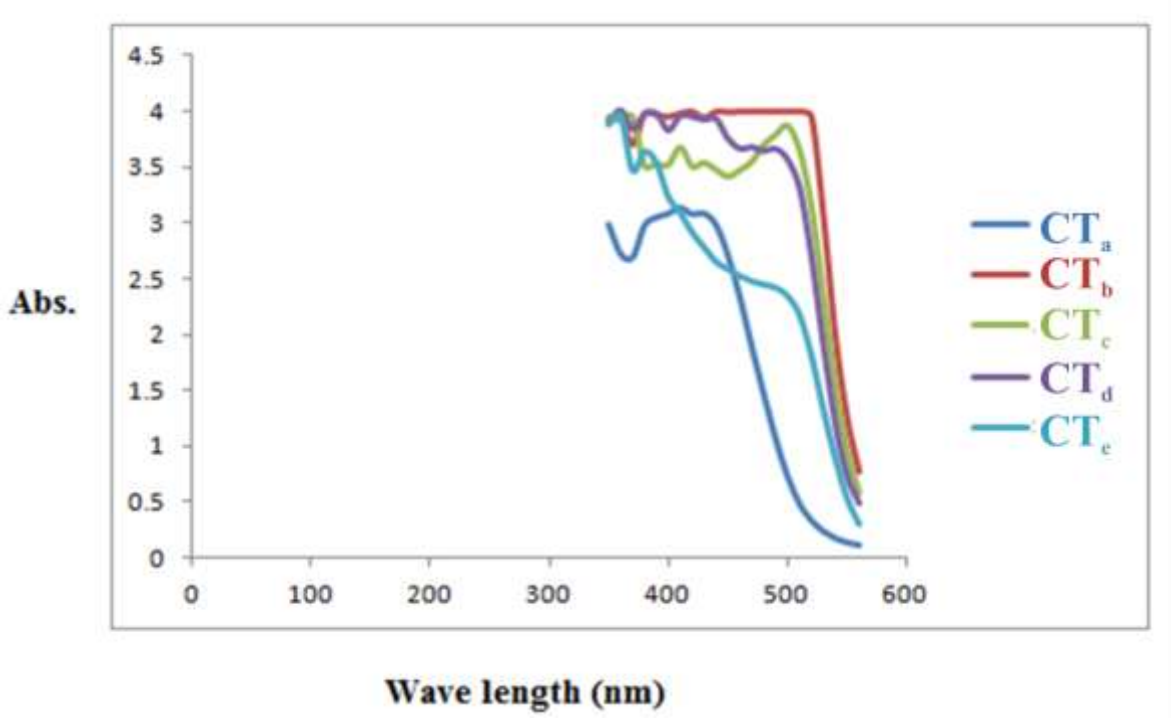


Figure 1: Electronic absorption spectra of the 1:1 CT-complexes (CTa-e) in DMSO

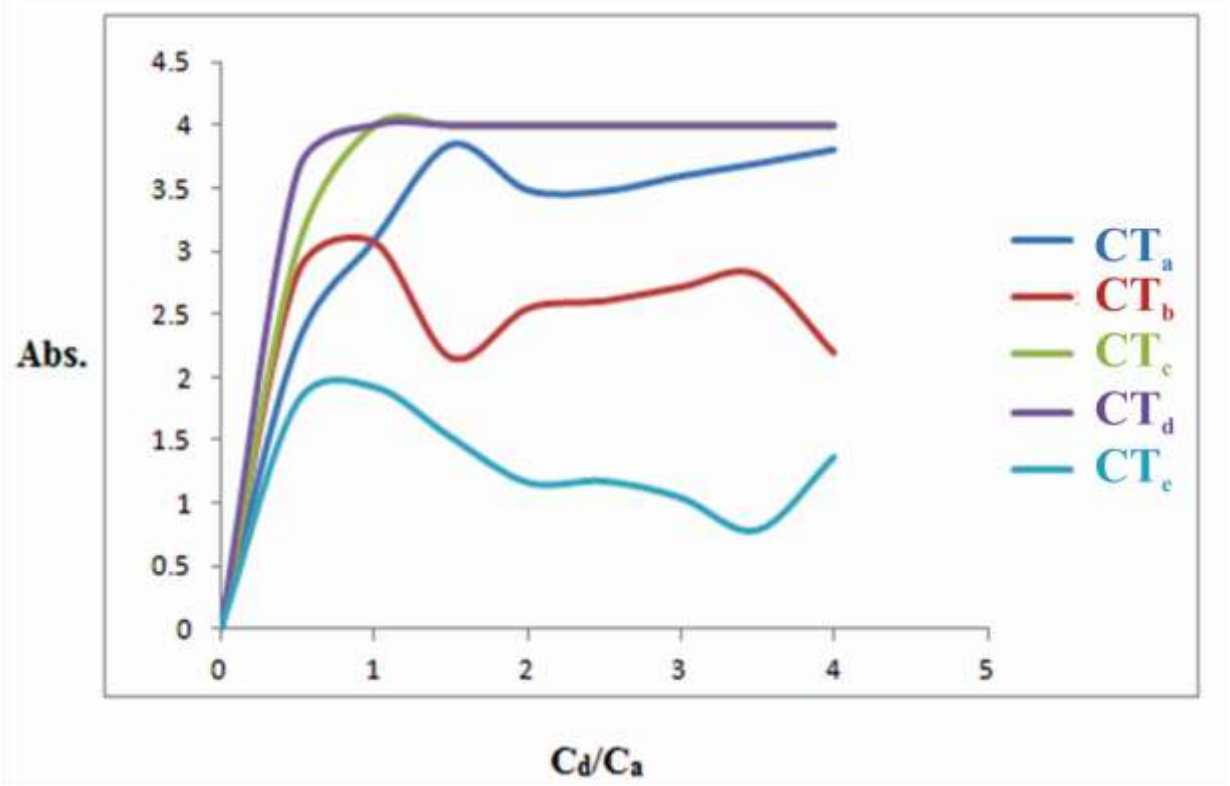


Figure 2: Spectrophotometric titration curve for the pyridine and amino substituted picoline: DMAD CT-complexes in DMSO at their corresponding λ_{max}

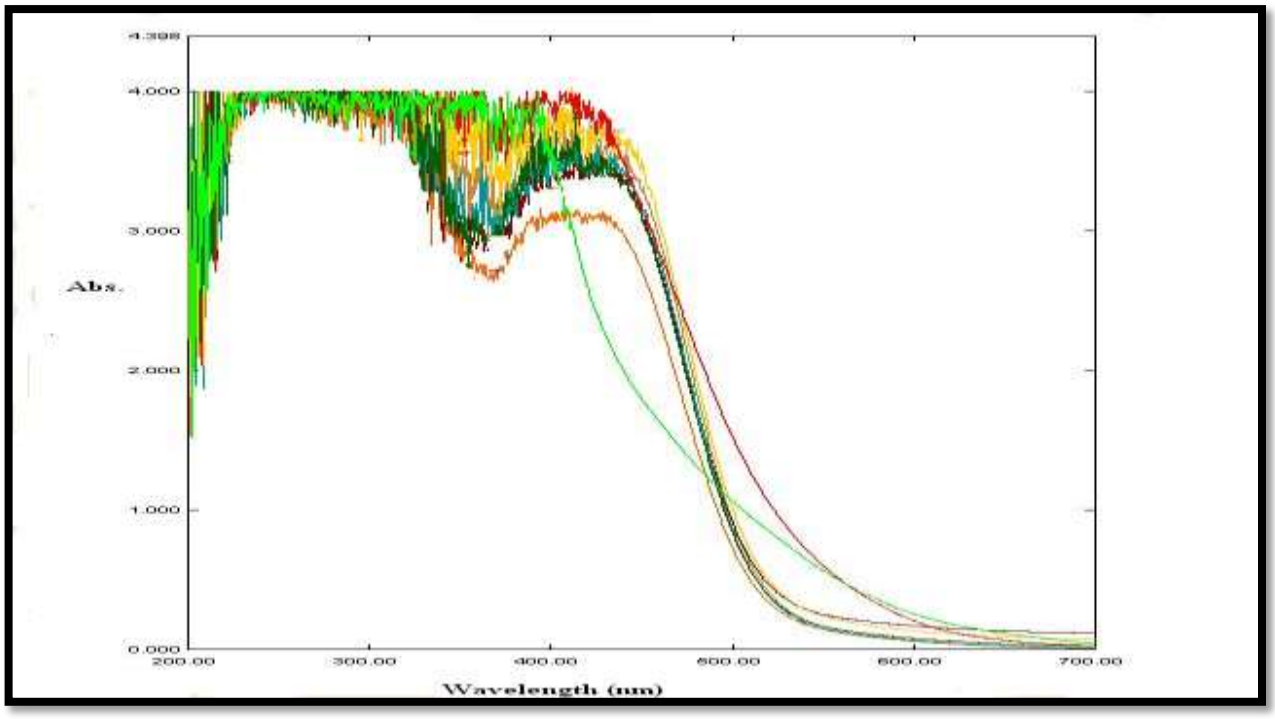


Figure 3: Electronic absorption spectra of CT-complex of pyridine (a) and DMAD in DMSO

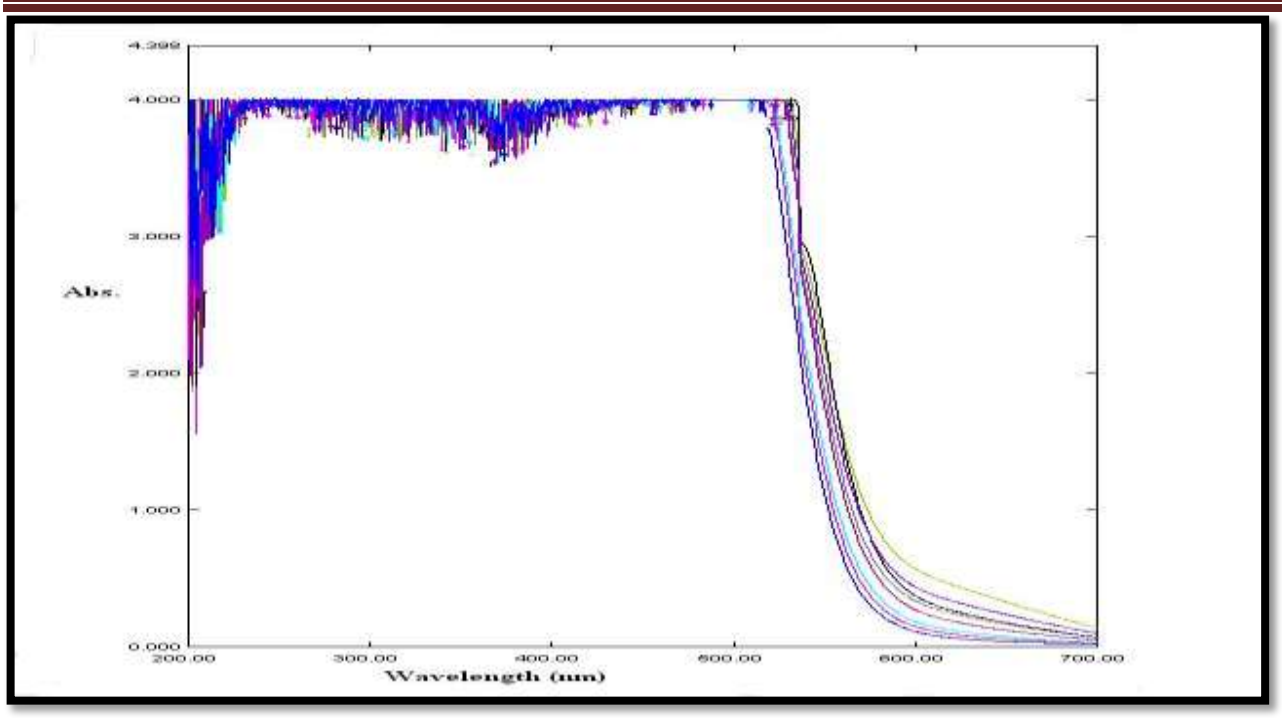


Figure 4: Electronic absorption spectra of CT-complex of 2-aminopyridine (b) and DMAD in DMSO

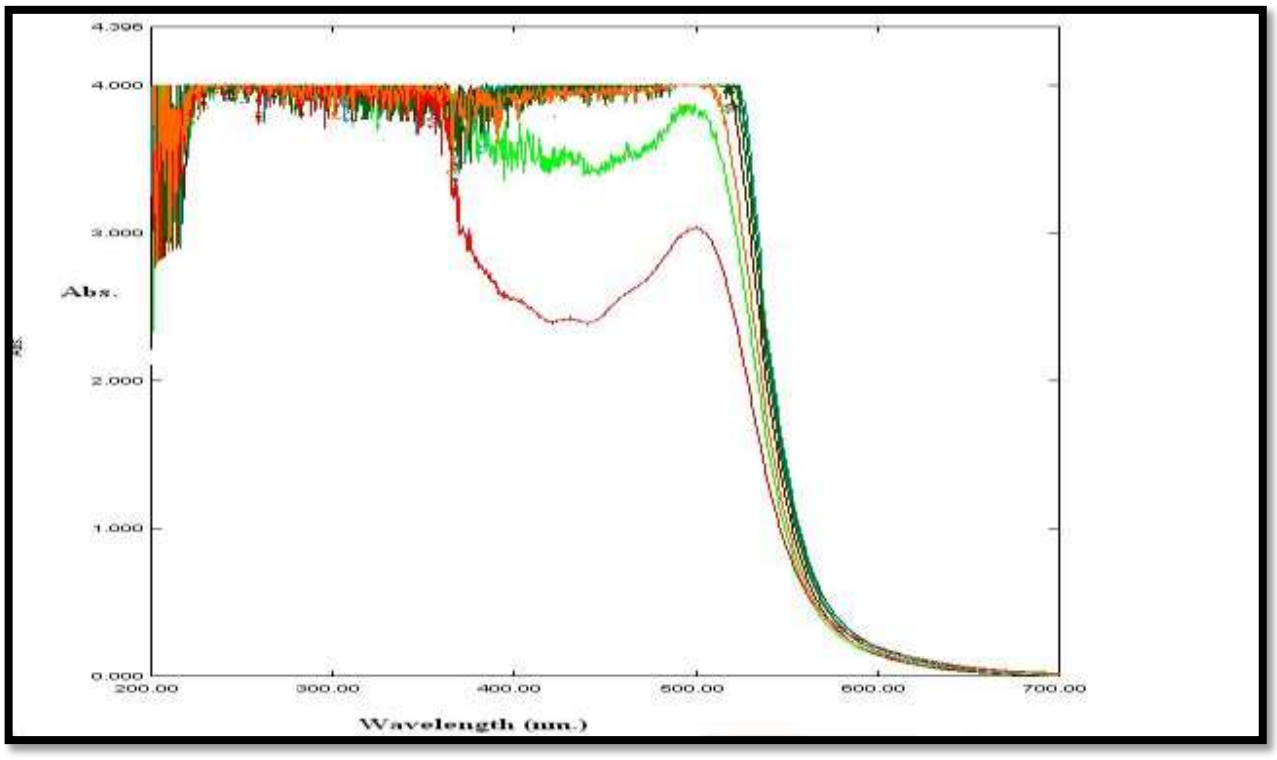


Figure 5: Electronic absorption spectra of CT complex of 2-amino-3-picoline (c) and DMAD in DMSO

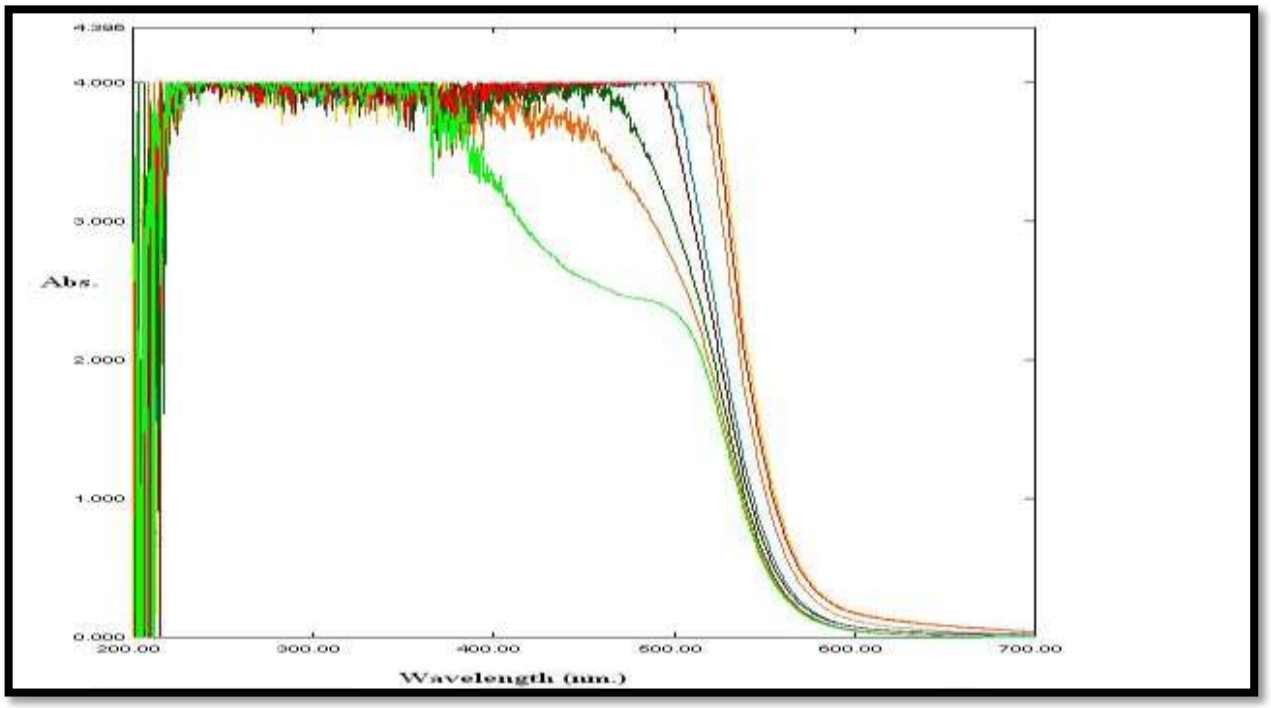


Figure 6: Electronic absorption spectra of CT-complex of 2-amino-4-picoline (d) and DMAD in DMSO

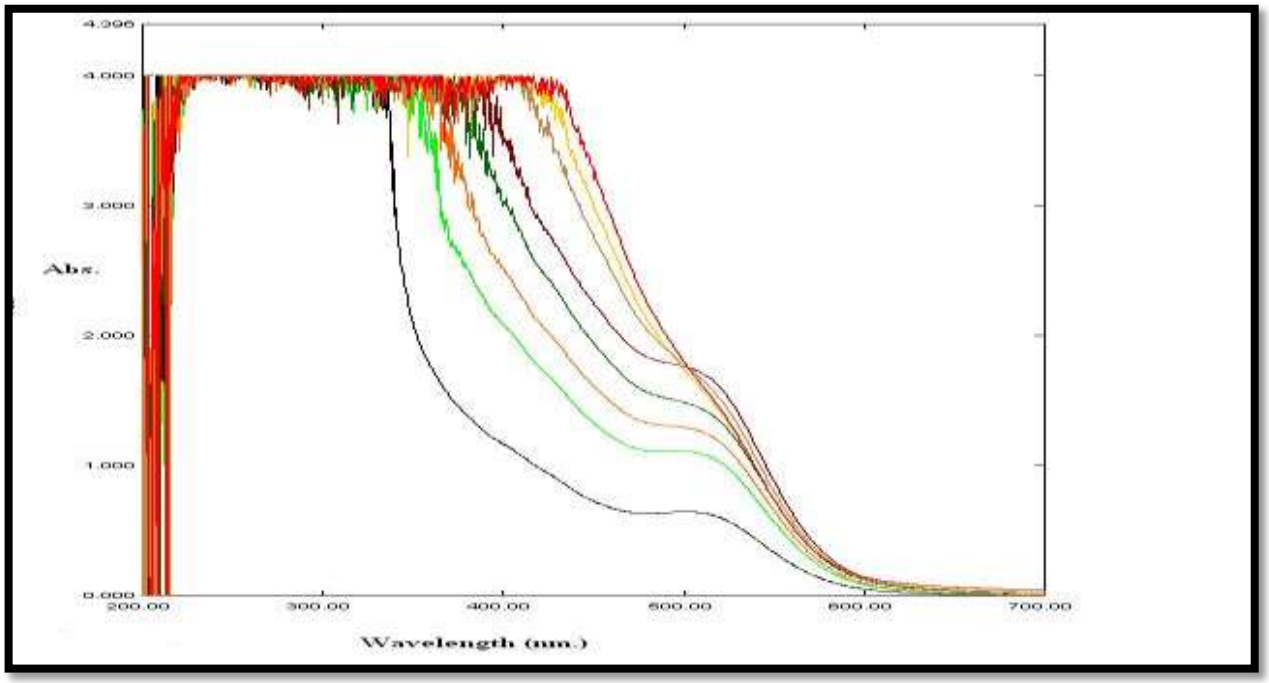


Figure 7:Electronic absorption spectra of CT complex of 2-amino-6-picoline (e) and DMAD in DMSO

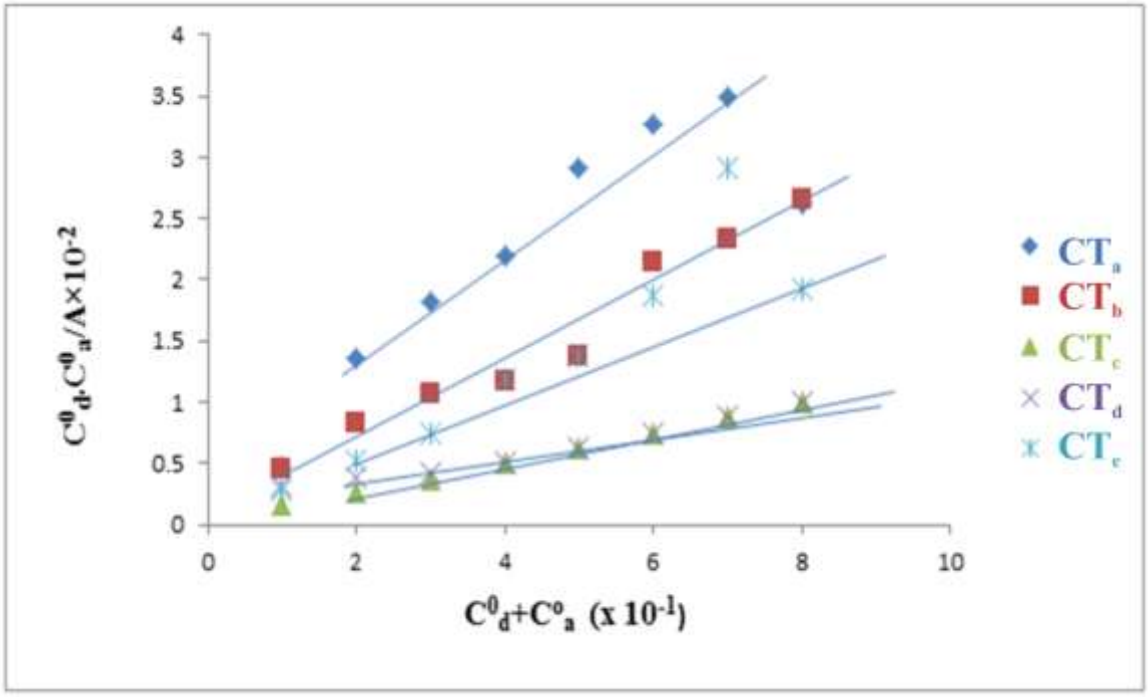


Figure 8: Spectral determination of the formation constants (K_{CT}) and molar extinction coefficients (ε_{CT}) of the 1:1 CT-complexes, CTa-e at their respective λ_{max}

The spectrophotometric data so obtained (Table 5) were used to calculate values of the equilibrium constant (K_{CT}) and the molar extinction coefficients (ε_{CT}) of the CT-complexes in

Table 5: The values of $C^0_d.C^o_a$ /A and $C^0_d+C^o_a$ for pyridine and it's amino derivatives and DMAD complexes

C^0_d (x10^{-1})	$C^0_d+C^o_a$ (x 10^{-1})	$C^0_d.C^o_a$ (x 10^{-2})	$C^0_d.C^o_a$/A(x 10^{-2}				
			CT_a (500nm)	CT_b (550nm)	CT_c (500nm)	CT_d (520nm)	CT_e (520nm)
0.50	1.50	0.50	0.471	0.448	0.165	0.312	0.277
1.00	2.00	1.00	1.367	0.833	0.259	0.384	0.526
1.50	2.50	1.50	1.818	1.070	0.375	0.416	0.750
2.00	3.00	2.00	2.192	1.170	0.500	0.500	1.183
2.50	3.50	2.50	2.906	1.380	0.625	0.625	1.380
3.00	4.00	3.00	3.275	2.150	0.750	0.750	1.875
3.50	4.50	3.50	3.500	2.330	0.875	0.875	2.910
4.00	5.00	4.00	2.630	2.660	1.000	1.000	1.930

DMSO for **CTa-e** having 1:1 stoichiometries using the modified Benesi-Hildebrand equation.

$$\frac{C^\circ_d . C^\circ_a}{A} = \frac{1}{\mathcal{E}K_{CT}} + \frac{C^\circ_d + C^\circ_a}{\mathcal{E}}$$

Where C^0_d and C^0_a are the initial concentration of the electron-donor and electron-acceptor, respectively and A is the absorbance of the CT band.

Plotting ($C^0_d.C^0_d$) × 10^{-2} versus ($C^0_d+C^o_a$) × 10^{-1} for the complexes **CTa-e**, straight line curves (Fig. 8**)** was obtained supporting the formation of the 1:1 complexes. With the help of these plots, the slope and intercept for each case was determined.

Slope = 1/ε and Intercept = 1/ε$K_{CT.}$ The values of the K_{CT} and ε associated with CT-complexes are given in Table 6. A high value of the formation constant, K_{CT} reflects higher stability of the formed CT-complex, which depends strongly on the nature of the donor. Thus a stability order of the synthesized CT-complexes may be predicted as follows.

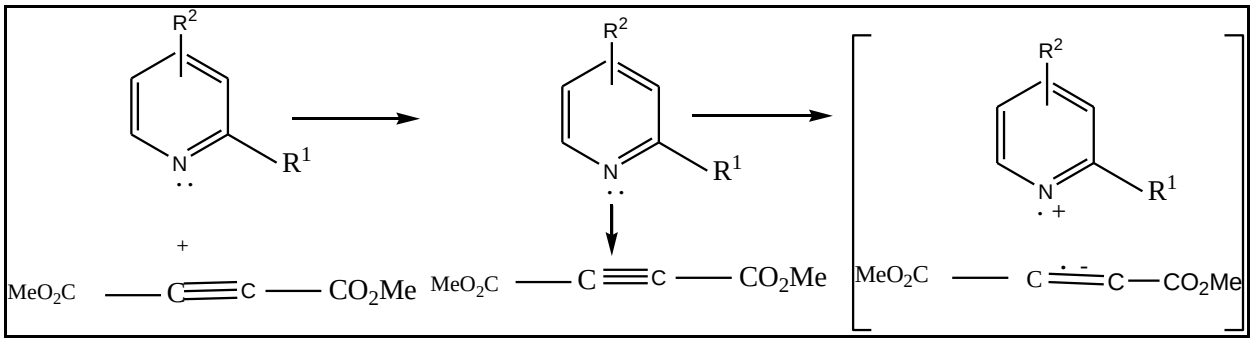
CT_d> CT_e>CTc>CT_b>CT_a

Table 6: Spectrophotometric results for 1:1 CT complexes

Complex	Slope of the curve	Intercept	$\mathfrak{E}_{CT}$	K_{CT}
CT_a	0.16	0.2	6.02	0.83
CT_b	0.20	0.1	5.00	1.33
CT_c	0.40	0.3	2.50	2.00
CT_d	0.95	0.1	1.05	9.50
CT_e	0.76	0.1	1.31	7.60

It is observed from the sequence given above that the CT complex formed by picolines has the higher values of $K_{CT,}$ predicts, higher stability than the CT complexes synthesized by pyridines and aminopyridines. The high stability of these complexes was expected from the high donation power of the donor due to the presence of two electron donating groups. Out of all the three picolines, 2-amino-4-picoline found to be little more stable than 2-amino-3-picoline and 2-amino-6-picoline. The least stability of 2-amino-3-picoline may be attributed to the less electron releasing effect produced by the methyl group due to its position, meta- to the nitrogen of the pyridine ring.The 2-amino pyridine formed more stable CT complex than pyridine.

The structure of CT complexes formed is predicted as follows-



R^1,R^2 = H, H; NH_2, H; NH_2, 3-Me; NH_2, 4-Me; NH_2, 6-Me

Conclusions

Charge transfer complexation between pyridine and its amino derivatives (donor) and dimethyl acetylenedicarboxylate (acceptor) has been studied spectrophotometrically in DMSO. The complex formation was confirmed from the appearance of the new wavelength band above 500 nm associated with colour change from colourless to red. The formation constant has been estimated by using Benesi-Hildebrand equation where it reached high value confirming high stability of the complex. The high stability of the CT complexes of 2-amino-4-picoline was expected from the high donation power of the donor due to the presence of two electron donating groups i.e. methyl and amino groups.

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