CHAPTER - 4

Spectrophotometric and spectroscopic studies of charge transfer complexes of p-toluidine as an electron donor with Picric acid as an electron acceptor in different solvents.

4.1. Introduction

Electron donor- acceptor (EDA) or charge transfer complexes (CT) are recently gaining importance as potential high efficiency non – linear optical materials [1], organic superconductors [2] as well as photo catalysts [3]. EDA interaction is also important in the field of drug – receptor binding mechanism [4] in solar energy storage [5] and in surface chemistry [6] as well as in many biological fields [7-9]. On the other hand, the charge transfer reactions of certain π- acceptors have been successfully utilized in pharmaceutical analysis [10-20]. For these wide applications extensive studies on CT complexes of π- acceptors have been performed [21-26].

Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene [27], some aniline derivative [28] and also with aromatic amines [29-31]. Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arise from the transfer of an electron from a π–molecular orbital of a Lewis base to vacant π- molecular orbital of a Lewis acid, with resonance between this dative structure and the no-bond structure stabilizing the complex [32]. He also noted the possibility of complex formation through the donation of an electron from a non- bonding molecular orbital in a Lewis base to a vacant π- orbital of an acceptor (n-π) [33] with resonance stabilization of the combination. As part of such studies charge transfer complex formation between picric acid (acceptor) and p-toluidine (donor) in different polar solvents have been investigated.

In this work, the study is focused on the interaction of PiOH (picric acid) with PTD (p-toluidine) in solvents of different polarity at room temperature by visible spectra data of CT complex of p-toluidine with π-acceptor, picric acid in solvents - carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol, and methanol and also studied the effect of solvents on the formation of CT complex. We have determined the formation constant and λ_{CT} for the CT complex of picric acid with p-toluidine in different solvents.

4.2. Chemistry of p- toluidine

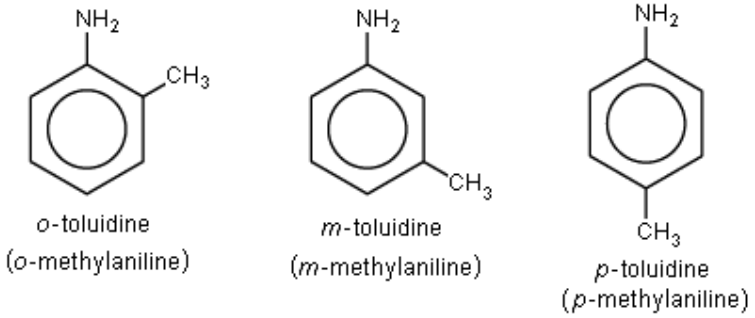
There are three isomers of toluidine. These isomers are o-toluidine, m-toluidine, and p-toluidine. The o- stands for ortho-, m- stands for meta-, and p- stands for para-. All three are aryl amines whose chemical structures are similar to aniline except that a methyl group is substituted onto the aromatic ring. The difference between these three isomers is the position where the methyl group (-CH_3) is bonded to the ring relative to the amino functional group (-NH_2).The chemical properties of the toluidines are quite similar to those of aniline and toluidines have properties in common with other aryl (often incorrectly referred to as aromatic) amines. Due to the amino group bonded to the aromatic ring, the toluidines are weakly basic. None of the toluidines is very soluble in pure water, but will become soluble if the aqueous solution is acidic. At room temperature and pressure, ortho- and meta-toluidines are viscous liquids, but para- toluidine is a flaky solid. This can be explained by the fact that the p-toluidine molecules are more symmetrical and fit into a crystalline structure more easily. p-toluidine can be obtained from reduction of p-nitrotoluene. p- toluidine reacts with formaldehyde to form Tröger's base. Toluidines are used in the production of dyes. They are a component of accelerators for cyanoacrylate glues. They are toxic and are suspected human carcinogens.

4.3. Experimental

4.3.1 Materials and Methods

p-toluidine (CDH), picric acid (Aldrich) were of the highest purity and used without further purification. Ethanol (Merck analytical grade), acetone (Merck), methanol (Merck) carbon tetrachloride (Merck), chloroform (Merck) and dichloromethane (Merck), were used without further purification.

Toluidine isomers			
Common name	o-toluidine	m-toluidine	p-toluidine
Other names	o-methylaniline 2-methylaniline	m-methylaniline 3-methylaniline	p-methylaniline 4-methylaniline
Chemical name	2-amino-1-methylbenzene	3-amino-1-methylbenzene	4-amino-1-methylbenzene
Chemical formula	C_7H_9N		
Molecular mass	107.17 g/mol		
Melting point	−23 °C	−30 °C	43 °C
Boiling point	199–200 °C	203–204 °C	200 °C
Density	1.00 g/cm^3	0.98 g/cm^3	1.05 g/cm^3
CAS number	[95-53-4]	[108-44-1]	[106-49-0]
SMILES	CC1=C(N)C=CC=C1	NC1=CC(C)=CC=C1	NC1=CC=C(C)C=C1



Toluidine Isomers

4.3.2 Preparation of standard solutions

Solutions of donor of different concentrations, .01 M, .015 M, .02 M, .03 M. .05 M, 0.1 M, 0.2 M, 0.3 M, and 0.5 M were prepared in different volumetric flask by dissolving p-toluidine accurately weighed in different solvents such as carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol.

A standard solution of acceptor, picric acid (0.01 M) concentration was prepared by dissolving accurate weight of acceptor in above solvents in different volumetric flask.

4.4. Results and Discussion

4.4.1 Observation of CT bands

The electronic absorption spectra of the donor p-toluidine, acceptor picric acid and the resulting complex in carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol were recorded in the visible range 400nm-600nm using a spectrophotometer ELICO SL 177 scanning mini spectrophotometer with a 1cm quartz cell path length.

A 3 ml volume of donor and acceptor were scanned separately through a spectrophotometric titration [34] at room temperature with their wavelength of maximum absorption 385 nm for picric acid, 440 nm for p-toluidine in acetone and for blank solvent (acetone) 340 nm shown in Fig 1. For the reaction mixture of donor (10 ml) and acceptor (10 ml) in different solvents viz carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol. A dark yellow color charge transfer complex was formed (The complex for each of the reaction mixture standing overnight at room temperature to form stable couple before analysis at the maximum absorbance (425 nm for carbon tetrachloride, 430 nm for chloroform, 435 nm for dichloromethane, 440 nm for acetone, 445 nm for ethanol and 450 nm for methanol). The electronic absorption spectra of PiOH and PTD in $CHCl_3$ and methanol are shown in Figures. (2 & 3). The concentration of the donor in the reaction mixture was kept greater than acceptor, $[D_0] >> [A_o]$ [35, 36] and changed

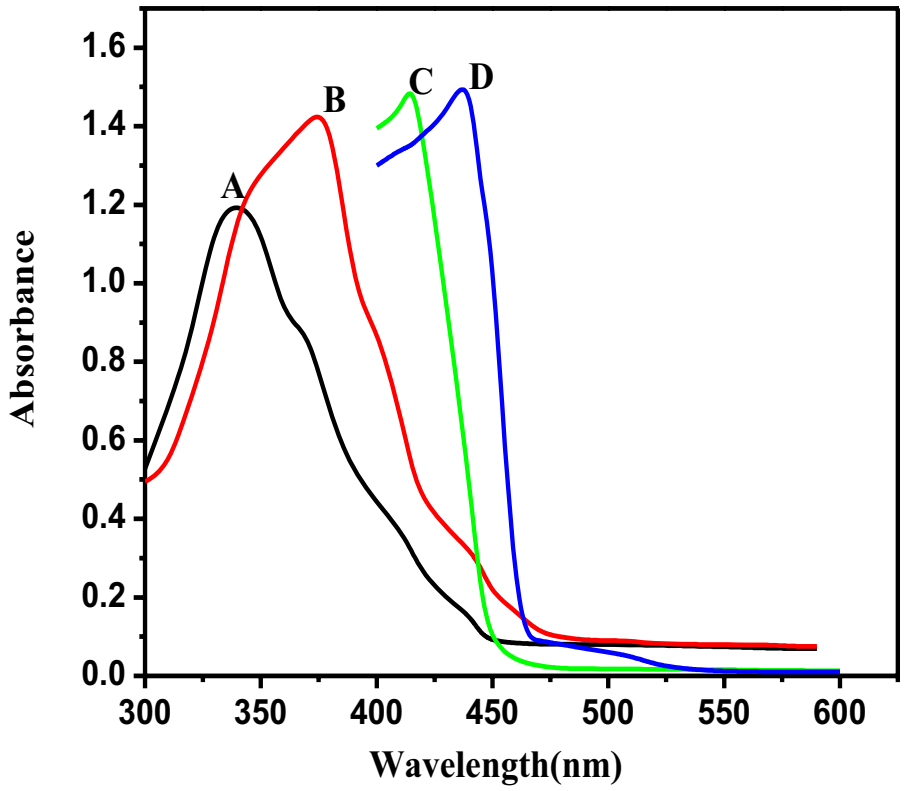


Fig. 1. Absorption spectra of (A) Blank solvent (acetone) (B) picric acid .01 M (C) p-toluidine .01 (D) CTC of PTD.01 M and PiOH .01 M in acetone

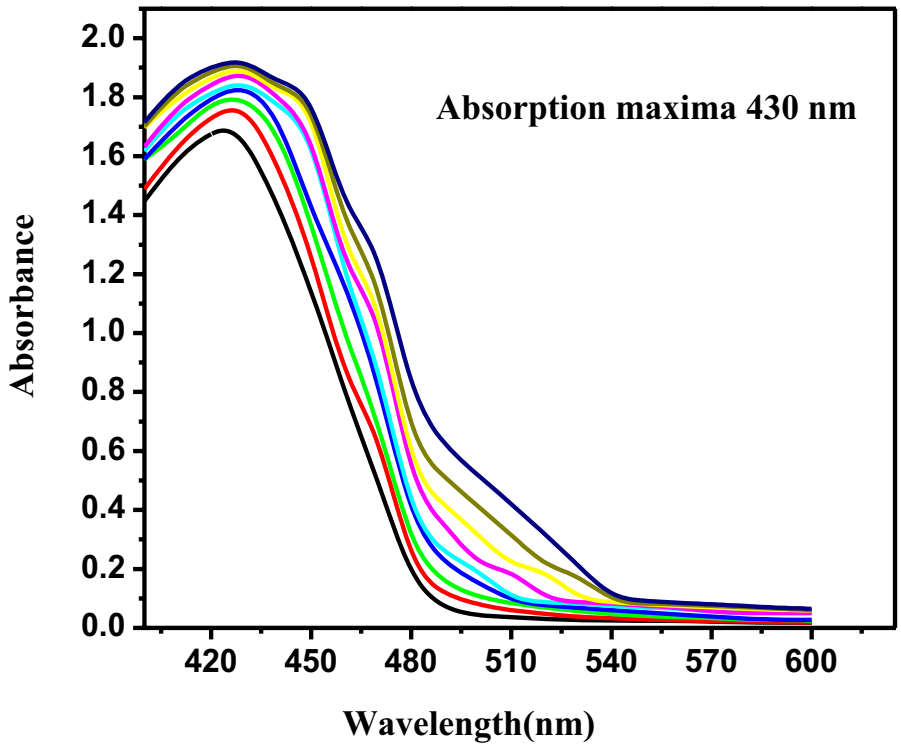


Fig. 2. Absorption spectra of picric acid (1×10^{-2} M) in chloroform with addition of p-toluidine concentrations ranging 0.01 M to 0.5 M are shown with increasing concentrations bottom to top.

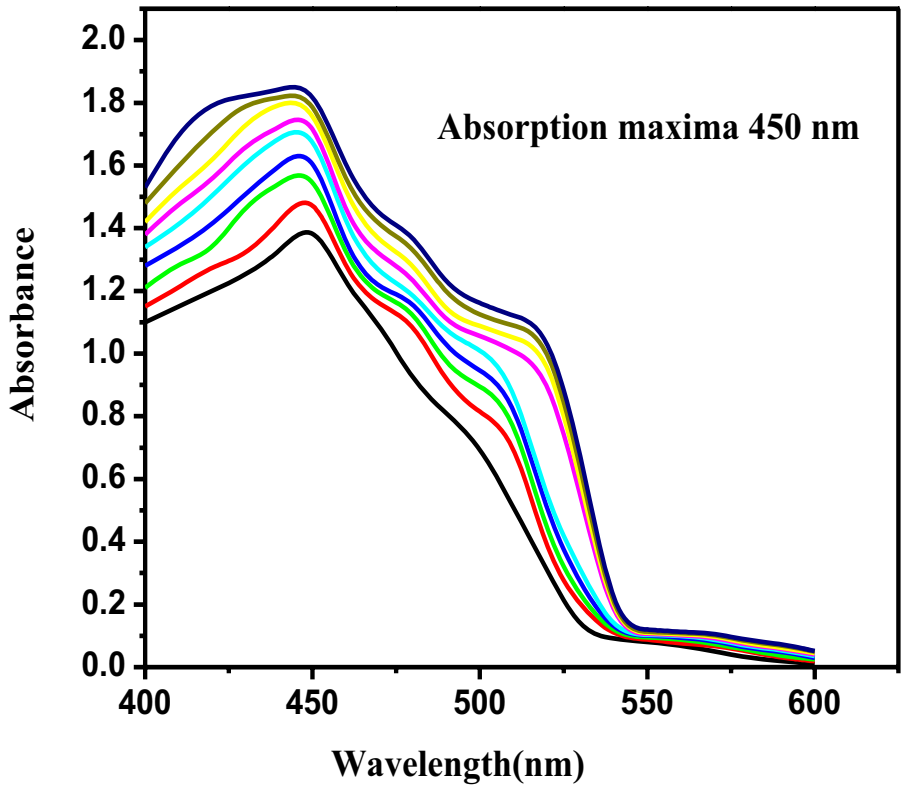


Fig. 3. Absorption spectra of picric acid (1×10^{-2} M) in methanol with addition of p-toluidine concentrations ranging 0.01 M to 0.5 M are shown with increasing concentrations bottom to top.

over a wide range of concentration from 0.01 M to 0.5 M while concentration of π-acceptor (picric acid) was kept fixed [35] at 0.01 M in each solvents, these produced solutions with donor: acceptor molar ratios varying from 1:1 to 50:1, these concentrations ratios were used to straight line diagram for determination of the formation constants of CTC.

To obtain the CT bands, the spectrum of solution of 0.01 M PiOH, and 0.01 M PTD in different solvents were recorded with solvents used as a reference, it is observed that new absorption peak appear in the visible region. In some cases multiple peaks were obtained, the longest wavelength peak was considered as CT peak [37] .The change of the absorption intensity to higher values for all complexes in this study when adding the donor was detected and investigated. These measurements were based on the CT absorption bands exhibited by the spectra of the systems mentioned above and given in Figures. (2 & 3).

In all systems studied the absorption spectra are of similar nature except for the position of absorption maxima (λ_{CT}) of the complex. The CTC absorption spectra were analyzed by fitting to the Gaussian function $y = y_0 + [A/ w\sqrt{(\pi/2)}] \exp [-2 (x- x_c)^2/w^2]$ where x and y denote wavelength and absorbance, respectively. The results of the Gaussian analysis for all systems under study are shown in Table 1. The wavelengths at these new absorption maxima ($\lambda_{CT} = x_c$) and the corresponding transition energies (hν) are summarized in Table 2.

4.4.2 Determination of Ionization potentials of the donor

The ionization potentials of the donor (I_D) in the charge transfer complexes are calculated using empirical equation derived by Aloisi and Piganatro [38].

$$I_D \text{ (eV)} = 5.76 + 1.53 \times 10^{-4} \quad \nu_{CT} \qquad (1)$$

where ν_{CT} is the wave number in cm^{-1} of the complex were determined in different solvents, viz, carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol.

Table 1 Gaussion curve analysis for the CTC in spectrum of PiOH with PTD different solvents

Systems	Area of the curve (A)	Width of the curve (W)	Centre of the curve (x_c)	Y_0
PiOH+PTD (carbon tetrachloride)	79.78 ± 4.43	38.022 ± 2.23	416.65 ± 0.930	0.01143 ± 0.02389
PiOH+PTD (chloroform)	131.76 ± 4.03	60.16 ± 1.91	421.10 ± 0.8977	0.00913 ± 0.0147
PiOH+PTD (dichloromethane)	123.10 ± 10.40	56.91 ± 4.74	423.62 ± 1.98	0.00019 ± 0.0433
PiOH+PTD (Acetone)	96.83 ± 9.18	47.95 ± 4.84	423.881 ± 1.905	0.00541 ± 0.0470
PiOH+PTD (Ethanol)	144.13 ± 18.56	78.62 ± 9.10	431.08 ± 3.66	-0.0233 ± 0.0646
PiOH+PTD (Methanol)	171.58 ± 10.94	99.93 ± 5.20	438.15 ± 1.85	-0.0167 ± 0.0341

Table 2 CT absorption maxima (λ_{CT}), transition energies ($h\nu_{CT}$), of the PiOH complexes, experimentally determined values of ionization potentials (I_D), oscillator strength (f), dipole moments (μ_{EN}), and resonance energies (R_N) of complexes

Systems	λ_{CT} (nm)	$h\nu_{CT}$(eV)	I_D(eV)	$f \times 10^5$	μ_{EN} (Debye)	R_N (eV)
PiOH+PTD (carbon tetrachloride)	416.65	2.98	9.43	1.52	0.917	.00713
PiOH+PTD (chloroform)	421.10	2.95	9.38	2.49	0.932	.00729
PiOH+PTD (dichloromethane)	423.62	2.93	9.37	2.42	0.944	.00742
PiOH+PTD (Acetone)	423.88	2.93	9.35	1.92	0.917	.00701
PiOH+PTD (Ethanol)	431.08	2.88	9.29	3.02	0.897	.00660
PiOH+PTD (Methanol)	438.15	2.83	9.24	3.99	0.914	.00674

4.4.3 Determination of oscillator strength (f) and transition dipole moment (μ_{EN})

From the CT absorption spectra, one can extract oscillator strength. The oscillator strength *f* is estimated using the formula

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT}\, d\nu \qquad (2)$$

where $\int \varepsilon_{CT} d\nu$ is the area under the curve of the extinction coefficient of the absorption band in question vs. frequency. To a first approximation

$$f = 4.32 \times 10^{-9}\, \varepsilon_{CT}\, \Delta\nu_{1/2} \qquad (3)$$

where ε_{CT} is the maximum extinction coefficient of the band and $\Delta\nu_{1/2}$ is the half- width, i.e., the width of the band at half the maximum extinction. The observed oscillator strengths of the CT bands are summarized in Table 2.

The extinction coefficient is related to the transition dipole by

$$\mu_{EN} = 0.0952\, [\varepsilon_{CT}\, \Delta\nu_{1/2}/\Delta\nu]^{1/2} \qquad (4)$$

where $\Delta\upsilon \approx \upsilon$ at ε_{CT} and μ_{EN} is defined as $-e \int \psi_{ex} \sum_i r_i \psi_g \, d\tau$. μ_{EN} for the complexes of PiOH with PTD are given in Table 2.

4.4.4 Determination of resonance energy (R_N)

Briegleb and Czekalla [39] theoretically derived the relation

$$\varepsilon_{CT} = 7.7 \times 10^{-4} / [h\nu_{CT}/ [R_N] - 3.5] \qquad (5)$$

where ε_{CT} is the molar extinction coefficient of the complex at the maximum of the CT absorption, ν_{CT} is the frequency of the CT peak and R_N is the resonance energy of the complex in the ground state, which, obviously is a contributing factor to the stability constant of the complex (a ground state property). The values of R_N for the complexes under study have been given in Table 2.

4.4.5 Determination of Standard free energy changes (ΔG^o), and transition energy (E_{CT}) of the π-π interaction between donor and acceptor*

The standard free energy changes of complexation (ΔG^o) were calculated from the association constants by the following equation derived by Martin, Swarbrick and Cammarata [40].

$$\Delta G^o = - 2.303\ RT \log K_{CT} \qquad (6)$$

where ΔG^o is the free energy change of the complexes (kJ mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}) T is the temperature in Kelvin degrees (273 + ^{0}C) and K_{CT} is the association constant of the complexes (l mol-^{1}) in different solvents at room temperature.

The energy (E_{CT}) of the π –π* interaction between donor (PTD), and acceptor, (PiOH), is calculated using the following equation derived by G. Briegleb and Z. Angew [41].

$$E_{CT} = \frac{1243.667}{\lambda_{CT} nm} \qquad (7)$$

where λ_{CT} is the wavelength of the CT band

4.4.6 Spectrophotometric *study of formation constants of the charge transfer complexes of PiOH/PTD in different solvents*

Stoichiometries and the formation constants of the charge transfer complex of p-toluidine with picric acid have been determined in different solvents viz- carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol at room temperature using Benesi–Hildebrand equation [42, 43]. The spectrophotometric data were employed to calculate the values of formation constants, K_{CT} of the complex. The changes in the absorbance upon addition of PTD to a solution of PiOH of fixed concentration follow the Benesi- Hildebrand [42, 43] equation in the form.

$$[A]_o / [A] = (1 / K_{CT}\varepsilon_{CT}) \times 1 / [D]_0 + 1/\varepsilon_{CT} \quad (8)$$

where $[D]_o$ and $[A]_o$ are the concentrations of the p-toluidine donor, and picric acid acceptor, respectively, A is the absorbance of the donor-acceptor mixture at λ_{CT}, against the solvents as reference, K_{CT} is the formation constant and ε_{CT} is the molar extinction coefficient, is not quite that of complex eq.(8) [42, 43] is valid under the condition $[D]_o >> [A]_o$ [35, 36] for 1:1 donor-acceptor complexes. The concentration of the donor (PTD) was changed over a wide range from 0.01 M to 0.5 M while concentration of π acceptor PiOH was kept fixed at 0.01 M in each reaction mixture. These produced solution with donor: acceptor molar ratio varying from 1:1 to 50:1, experimental data are given in Tables 3 and 4.

The Benesi – Hildebrand [42, 43] method is an approximation that has been used many times and gives decent results. But the extinction coefficient is really a different one between the complex and free species that absorbs at the same wavelength. The intensity in the visible region of the absorption bands, measured against the solvent as reference, increases with increased in the polarity and addition of PTD. The typical absorbance data for charge transfer complexes of PTD with PiOH in different solvents at room temperature are reported in Table 3 and 4. In all systems very good linear plots according to eq. (7) [42, 43] are obtained, the linear plot of PiOH + PTD in carbon tetrachloride, chloroform, and methanol shown in Figs. (4, 5 & 6) Formation constants for the complex in different polar solvents at room temperature determined from the BH plots are summarized in Tables 3 and 4. The correlation coefficients of all such plots were above than 0.994. Plots of $[A]_0/[A]$ against $1/[D]_o$ were found to be linear in all systems in some example shown in Figs. 4, 5 & 6 showing 1:1 charge transfer complex, i.e. the straight lines are obtained with the slopes $1/K_{CT}\varepsilon_{CT}$, these results prove the formation of the 1:1 CTC. From slope $1/K_{CT}\varepsilon_{CT}$ and intercept, $1/\varepsilon_{CT}$, K_{CT} and ε_{CT} of the complex were calculated.

4.4.7 Effect of solvents on the formation of CT- complexes

The experimental results of the CT interaction between PiOH with PTD in different solvents show the values of association constants K_{CT} 881($1mol^{-1}$) in

carbon tetrachloride, 796 ($1mol^{-1}$) in chloroform, 604 ($1mol^{-1}$)in dichloromethane, 502 ($1mol^{-1}$) in acetone, 432 ($1mol^{-1}$) in ethanol, and 360 ($1mol^{-1}$) in methanol and the values of molar extinction coefficient ε_{CT} 186 ($1mol^{-1}cm^{-1}$) in carbon tetrachloride, 192 ($1mol^{-1}cm^{-1}$) in chloroform, 197 ($1mol^{-1}cm^{-1}$)in dichloromethane, 186 ($1mol^{-1}cm^{-1}$) in acetone, 178 ($1mol^{-1}cm^{-1}$) in ethanol and 185 ($1mol^{-1}cm^{-1}$) in methanol and spectroscopic properties were markedly affected by the variation in solvent polarity in which measurements were carried out. In the present investigation the K_{CT} values increases significantly from methanol to carbon tetrachloride with decreasing solvents polarity. Moreover, the increase in K_{CT} values with decreasing solvents polarity, may also be due to the fact that, CTC should be stabilized in non polar solvent [44]. Dissociation of the complexes into D^{+} ——A^{-} radicals have been found to occur in the ground state [45]. It means the CTC should be strong in non polar solvent than polar solvent. The red shift occurred in CTC complex caused by polarity change on going from carbon tetrachloride to methanol.

However the data given in Tables 3 and 4 shows that PiOH interacts more strongly with PTD in carbon tetrachloride than other solvents. The experimentally determined values of oscillator strength (f) 1.52×10^{-5} in carbon tetrachloride, 2.49×10^{-5} in chloroform, and 2.42×10^{-5} in dichloromethane, 1.92×10^{-5} in acetone, 3.02×10^{-5} in ethanol and 3.99×10^{-5} in methanol and the values of transition dipole moment (μ_{EN}) 0.917(Debye) in carbon tetrachloride, 0.932 (Debye) in chloroform and 0.944 (Debye) in dichloromethane, 0.917 (Debye) in acetone, 0.897 (Debye) in ethanol and 0.914 (Debye) in methanol values of resonance energy(R_N) 0.00713 (eV) in carbon tetrachloride, 0.00729 (eV) in chloroform, 0.00742 (eV) in dichloromethane, 0.00701(eV) in acetone, 0.0066 (eV) in ethanol and 0.00674 (eV) methanol given in Table 2 indicate that complex should be stable in non polar solvent (carbon tetrachloride) than other solvents. The very low values of f indicate that CT complex studied here have almost neutral character in their ground state.

Table 3 Data for spectrophotometric determination of stoichometry, absorption maxima (λ_{CT}), and association constants (K_{CT}), molar absorptivities (ε_{CT}), of CTC of PiOH and PTD in different polar solvents at 298 K

Systems	Temperature (K)	Donor concentration M	$[A]_0$ M	Absorbance at λ_{CT} (nm)	λ_{CT} (nm)	K_{CT} ($lmol^{-1}$)	ε_{CT} ($1mol^{-1}$ cm^{-1})
PiOH/PTD (carbon tetrachloride)	298	0.01	0.01	1.677	425	881	186
		0.015		1.732			
		0.02		1.754			
		0.03		1.785			
		0.05		1.812			
		0.1		1.835			
		0.2		1.853			
		0.3		1.861			
		0.5		1.868			
PiOH/PTD (chloroform)	298	0.01	0.01	1.710	430	796	192
		0.015		1.783			
		0.02		1.805			
		0.03		1.845			
		0.05		1.860			
		0.1		1.895			
		0.2		1.908			
		0.3		1.924			
		0.5		1.932			
PiOH/PTD (dichloromethane)	298	0.01	0.01	1.691	435	604	197
		0.015		1.782			
		0.02		1.812			
		0.03		1.858			
		0.05		1.898			
		0.1		1.932			
		0.2		1.945			
		0.3		1.964			
		0.5		1.987			

Table 4 Data for spectrophotometric determination of stoichometry, absorption maxima (λ_{CT}), and association constants (K_{CT}) molar absorptivities (ε_{CT}) of CTC of PiOH and PTD in different non polar solvents at 298 K

Systems	Temperature (K)	Donor concentration M	$[A]_0$ M	Absorbance at λ_{CT} (nm)	λ_{CT} (nm)	K_{CT} ($lmol^{-1}$)	ε_{CT} ($1mol^{-1}$ cm^{-1})
PiOH/PTD (Acetone)	298	0.01	0.01	1.558	440	502	186
		0.015		1.635			
		0.02		1.698			
		0.03		1.740			
		0.05		1.787			
		0.1		1.829			
		0.2		1.840			
		0.3		1.852			
		0.5		1.870			
PiOH/PTD (Ethanol)	298	0.01	0.01	1.454	445	432	178
		0.015		1.542			
		0.02		1.595			
		0.03		1.650			
		0.05		1.710			
		0.1		1.744			
		0.2		1.762			
		0.3		1.779			
		0.5		1.795			
PiOH/PTD (Methanol)	298	0.01	0.01	1.440	450	360	185
		0.015		1.540			
		0.02		1.610			
		0.03		1.677			
		0.05		1.740			
		0.1		1.788			
		0.2		1.812			
		0.3		1.842			
		0.5		1.871			

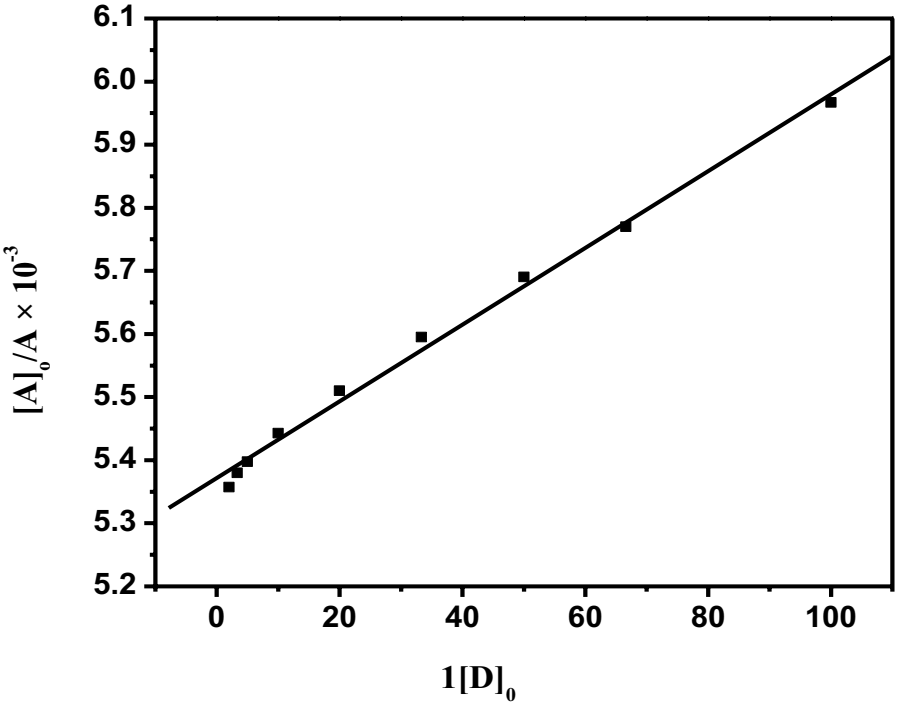


Fig. 4. Relation between $[A]_0/A$ and $1/[D]_0$ of PiOH + PTD in carbon tetrachloride

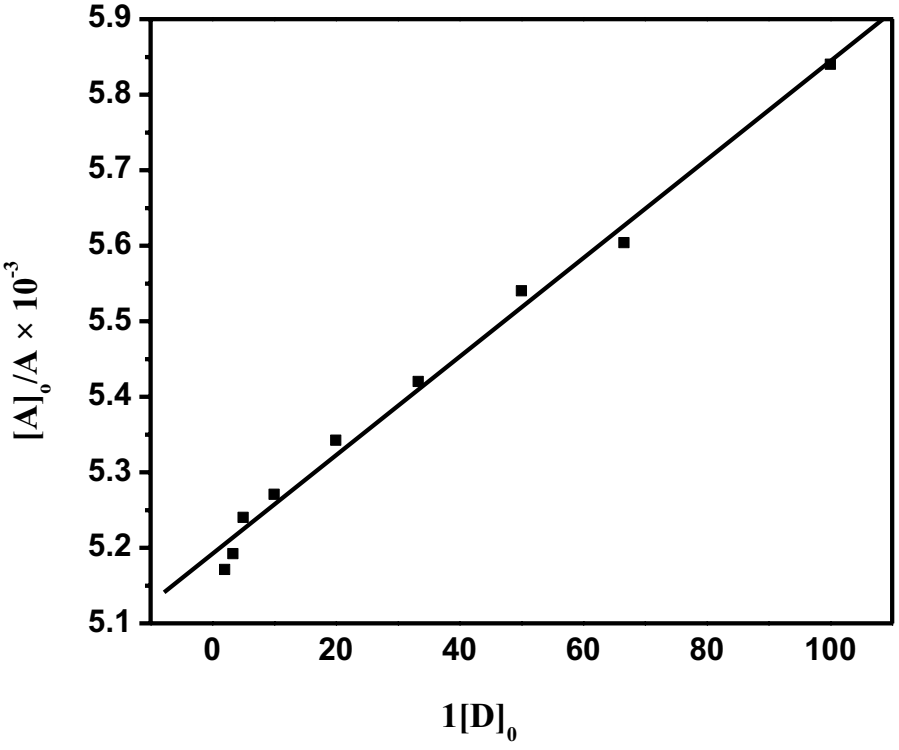


Fig. 5. Relation between $[A]_0/A$ and $1/[D]_0$ of PiOH +PTD Chloroform.

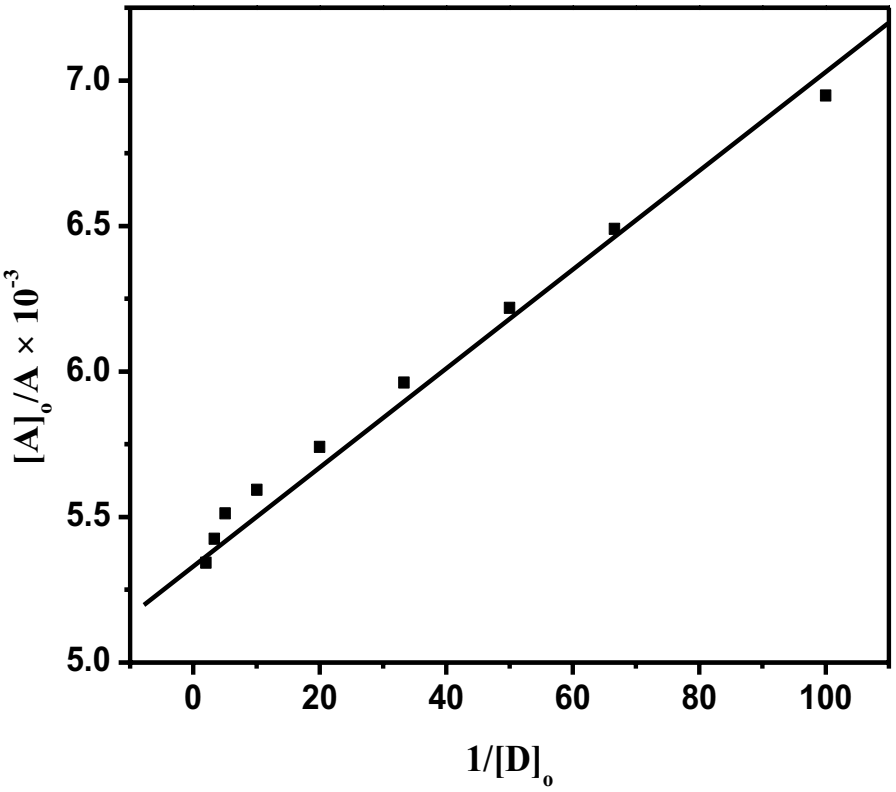


Fig. 6. Relation between $[A]_0/A$ and $1/[D]_0$ of PiOH and PTD in methanol.

The parameters thus obtained are represented in Table 5 and these values show that complexation is thermodynamically favored. The free energy change of the complexation also reveals that the CTC formation between used donor (PTD) and acceptor (PiOH) is of exothermic in nature. The values of ΔG^0 -16.775 ($kJmol^{-1}$) in carbon tetrachloride,-16.546 ($kJmol^{-1}$) in chloroform,-15.862 ($kJmol^{-1}$) in dichloromethane,-15.405 ($kJmol^{-1}$) in acetone, -15.006 ($kJmol^{-1}$) in ethanol, and -14.549 ($kJmol^{-1}$) in methanol given in Table 5 generally become more negative as the association constants for molecular complex increases. As the bond between the components becomes stronger and thus the components are subjected to more physical strain or loss of freedom, the values of ΔG^o more negative.

The ionization potentials I_D (eV) of the donor can be calculated using the experimentally determined λ_{CT} of the CTC from eq. (1) [38]. The calculated values of I_D 9.35 (eV) in carbon tetrachloride, 9.30 (eV) in chloroform, 9.26 (eV) in dichloromethane, 9.23 (eV) in acetone, 9.19 (eV) in ethanol, and 9.15 (eV) in methanol of PiOH/PTD system are shown in Table 6. The approximate constancy of I_D values, indicates that the ionization potential show a negligibly small effect on K_{CT} values.

4.4.8 Comparative study of FT-IR spectra of CT complex and reactants

FT-IR spectra of picric acid, p-toluidine and the reaction product obtained from solid state reaction between acceptor and donor were recorded with the help of FT-IR spectrometer INTERSPEC–2020 (spectra lab U.K.) measured in KBr pellets. FT-IR spectra of the free acceptor and donor as well as the formed CT complex are shown in Fig. 7 and their bands assignments reported in Table 7. However the appearance of a group of FT-IR spectral bands in the spectra of CT complex support the conclusion that a deformation of the electronic environment of p-toluidine has occurred by accepting a proton from PiOH. The shift of the FT-IR bands of the acceptor to lower wave numbers and those of the donor part to higher values reflects a donor to acceptor charge transfer of π-π* interaction , $D_{HOMO} \rightarrow A_{LUMO}$ transition [46].

Table 5 Association constant (K_{CT}), correlation coefficients (r) and standard free energy changes (ΔG^o) of PiOH/PTD complexes obtained from Benesi-Hildebrand plots

Systems	K_{CT} ($lmol^{-1}$)	$-\Delta G^o$(298K) ($k_J mol^{-1}$)	r
PiOH/PTD (carbon tetrachloride)	881	16.775	0.996
PiOH/PTD (chloroform)	796	16.546	0.995
PiOH/PTD (dichloromethane)	604	15.862	0.994
PiOH/PTD (Acetone)	502	15.405	0.997
PiOH/PTD (Ethanol)	432	15.006	0.998
PiOH/PTD (Methanol)	360	14.549	0.998

Table 6 The CTC transition energies (E_{CT}), CTC absorption maxima (λ_{CT}), and Ionization potential (I_D) of donor of in different solvents

Systems	E_{CT} (eV)	λ_{CT} (nm)	I_D (eV)
PiOH/PTD (carbon tetrachloride)	2.92	425	9.35
PiOH/PTD (chloroform)	2.89	430	9.30
PiOH/PTD (dichloromethane)	2.85	435	9.26
PiOH/PTD (Acetone)	2.82	440	9.23
PiOH/PTD (Ethanol)	2.79	445	9.19
PiOH/PTD (Methanol)	2.76	450	9.15

The FT-IR spectrum of the complex of PiOH and PTD in Fig 7 shows the presence of characteristic absorption bands due to the varied forced constants in the donor and the acceptor species on account of the prevalent charge transfer mechanism. This makes the crystals of this type more ionic than other organic crystals. In the FT-IR spectra of the complex the O-H and N-H stretching vibrations are observed at 3235.17cm^{-1} and 3085.39 cm^{-1} respectively. The band at 2925.27cm^{-1} is due to the aromatic C-H stretching vibration. The -NH_2 deformation mode is observed by the absorption at 1628.79cm^{-1}. This band overlaps with the aromatic C=C stretching vibrations. The asymmetric and symmetric stretching vibrations of the –NO_2 group are observed at 1561.64cm^{-1} and 1370.53cm^{-1} respectively. Normally the asymmetric stretching vibration of the –NO_2 group is sensitive to polar influences and the electronic states of the species. Therefore, it has been realized that the shift to lower frequency of ν_{asym} (NO_2) vibration (1561.64cm^{-1}) in the spectrum of the complex compared with free picric acid (1606 cm^{-1}) is due to the increased electron density on the picric acid moiety owing to the charge transfer interaction in the complex [47]. The absorption at 1628.79$cm^{-1,}$ 1561.64cm^{-1}, 1509.99and 1437.68cm^{-1} are due to the aromatic C = C absorption stretching vibrations. The absorption at 1267.22$cm^{-1}$is due to the C-N stretching vibration. The C-O stretching vibration is observed as a band of medium intensity at 1163.92cm^{-1}.The C-H in plane bending vibration is observed at 1081.28cm^{-1} and the C-H out of plane bending is evidenced by the presence of a band at 789.95cm^{-1}. The C-NO_2 stretching is observed at 936.65cm^{-1}. The NO_2 wagging vibrations are observed at 734.26$cm^{-1}$and 789.95cm^{-1}. The band at 699.05cm^{-1} is due to the ring bending vibration. The assignments of various absorption frequencies of the compound are given in Table 7. In the spectra of CT- complex of p-toluidine and picric acid, PTD almost completely consumed evidence of H- bonding and –OH intensity decreased and position of the peak also shifted.

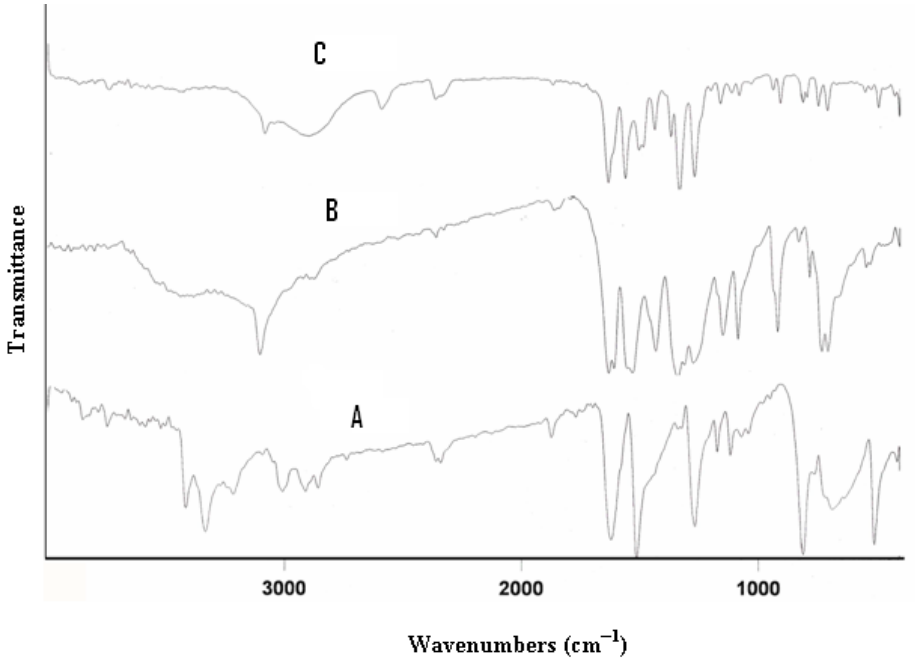


Fig.7.FT-IR spectra of (A) p-toluidine (donor) (B) picric acid (acceptor) and (C) CT complex.

Table 7 Characteristic infrared frequencies (cm^{-1}) and tentative assignments for PiOH, PTD and their complex.

PiOH	PTD	Complex	Assignments
3108 s, br	3410sharp	3235sh	ν(O-H) ,H bonded
-	3338 br	3083sharp	ν (N-H)
-	3211br	-	
	3013 br	-	
	2909br	2890br	ν (C-H)
2875 w	2855w	2589br	
	2357sharp	2362w	ν_{as} (C-H)
1630 vs	1618vs	1628ms	ν_s (NO_2)
1606ms			ν_S (C=N)
1529 br	1515vs	-	ν(C=C)
	-	1561ms	δ def (N-H), $+NH_2$ ring breathing bands
	-	1509ms	
1437ms		1437vs	C-H deformation
-	1340sh	1370br	ν(C-C), $\nu_s NO_2$
1341vs		-	ν(C-N)
1275vs	1267vs	1267br	ν(C-O)
1154ms	1174w		
	1117w	1163ms	(C-H) in plane bending
1083ms	1040br		
	-	1081ms	
916ms	-	936sharp	δrock , $+NH_2$
830w		812sharp	
779sharp	812sharp		$CH_{2\ rock}$ skeletal vibrations
	735vs	745vs	
734ms	678vs	-	C-H out of plane bending
703ms	-		
663w	507ms	699vs	
546w	480ms	541sh	δ(ONO), PiOH
521w	-	482sharp	CNC deformation
419sharp	404sharp	409ms	

S, strong, w, weak ; m, medium , sh , shoulder , v , very ; vs, very strong , br, broad ; ν, stretching; ν_s, symmetrical stretching ; ν_{as}, asymmetrical stretching

4.4.9 ^{1}H NMR Spectrum of complex

The nuclear magnetic resonance, ^{1}H NMR spectrum of CT complex is measured in DMSO using Bruker Advance II 400 NMR spectrometer is shown in Fig 8. The spectrum of CT complex was compared with the reactants and the chemical shifts (δ) of the different types of protons of the donor, acceptor and CT complex are listed in Table 8.

The singlet at δ = 9.721ppm is due to –OH proton of picric acid in the complex. The same was observed at δ = 11.94ppm in the free picric acid [48]. This up field shift is due to the shielding of the –OH proton by the π electrons and n electrons of p- toluidine. The singlet peak at δ = 8.598ppm has been assigned to the two protons of the same kind in picric acid moiety in the complex whereas in free picric acid this was observed at 8.57ppm. The doublet peaks at δ = 7.31ppm and 7.28ppm are assigned to the proton on C_2, C_3, C_5 and C_6 carbon atom of p- toluidine moiety in the complex. The same were observed at δ = 6.67ppm and δ = 6.861ppm in free p- toluidine. These shifts assume that the amino group and phenolic group are mainly involved in the formula of the CT complex.

Table 8 ^{1}H NMR Spectral data of complex.

Chemical shift values (δ) in ppm	Assignments
9.721(s)	OH proton of picric acid in the complex
8.59(s)	Two protons of the same kind in the picric acid moiety in the complex.
7.31(d)	C_2 proton of p- toluidine in the complex
7.28(d)	C_3 proton of p- toluidine in the complex
7.23 (d)	C_5 proton of p- toluidine in the complex
7.21(d)	C_6 proton of p- toluidine in the complex

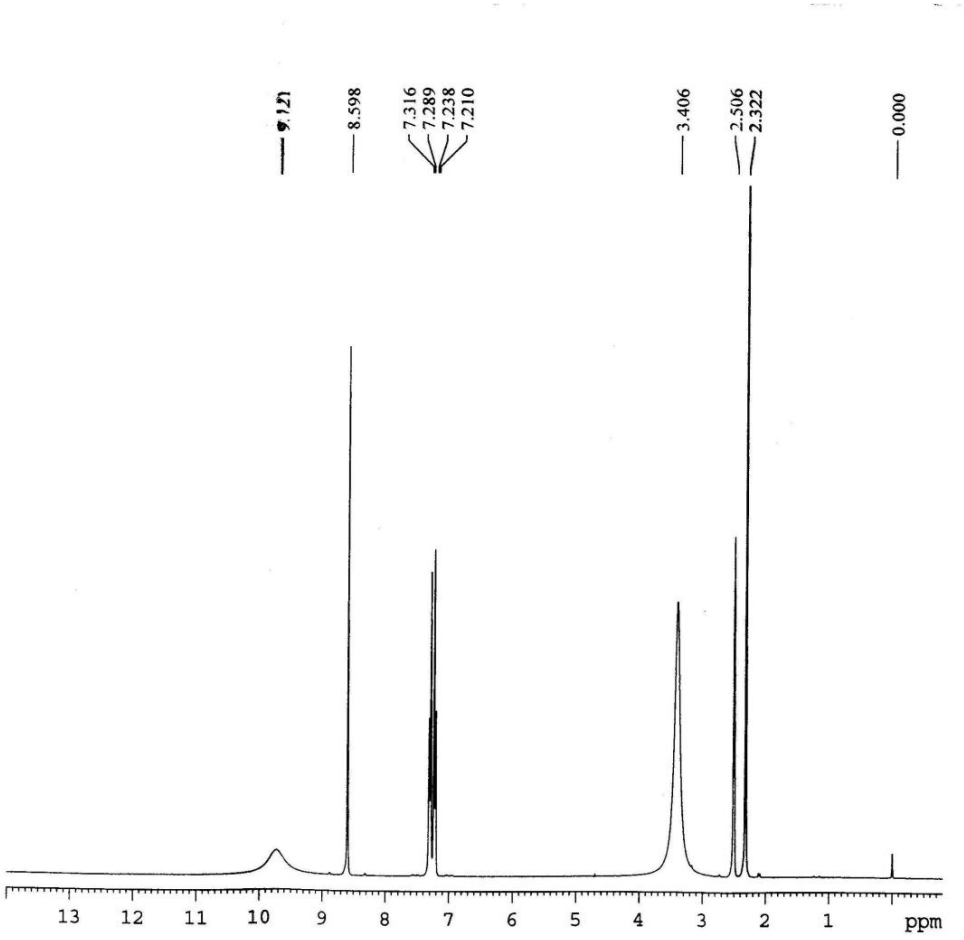


Fig. 8. ^{1}H NMR Spectrum of complex

Conclusions

From the foregoing discussion, it may be concluded that the UV –Vis spectrophotometric method for the study of CTC of picric acid with p-toluidine reveals that it forms 1:1 (A: D) complex in all solvents, viz – carbon tetrachloride, chloroform, dichloromethane, acetone, ethanol and methanol. In all systems the stoichiometry is unaltered by changing the solvent. The association constants, K_{CT} and molar extinction coefficients, ε_{CT} of all systems were evaluated by the Benesi - Hildebrand method. The values of association constant of the CTC decrease with increasing solvent polarity, due to the destabilization of CTC in polar solvents and then the dissociation of the complex into $D^+ A^-$. The interaction between the donor and acceptor was found to be π-π^* transitions by the formation of radical ion pairs. The spectroscopic and thermodynamic parameters of the complexes were found to be solvents dependent. The values of oscillator strengths (*f*) transition dipole moments (μ_{EN}) resonance energies (R_N) and standard free energies (ΔG^o) have been estimated for the PiOH/PTD systems in different solvents. The results show that the investigated complex is stable, exothermic and spontaneous. From the trends in the CT absorption bands, the ionization potentials of the donor molecules have been estimated. The FT-IR spectrum shows that the complex formed between donor and acceptor by transferring a proton from acceptor (PiOH) to donor (PTD).

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