CHAPTER - 2

Spectrophotometric study of the charge transfer complexation of picric acid (2, 4, 6 tri nitro phenol) as an electron acceptor with p-nitroaniline as an electron donor

2.1. Introduction

Mulliken's theory of charge transfer interactions between an electron donor and electron acceptor [1, 2] has been successfully applied to many interesting studies [3]. Charge –transfer complexes are known to take part in many chemical reactions like addition, substitution and condensation [4, 6]. These complexes have attracted great attention for non- linear optical materials and electrical conductivities [7-10]. Electron donor-acceptor (EDA) interaction is also important in the field of drug – receptor binding mechanism [11], in solar energy storage [12] and in surface chemistry [13] as well as in biological fields [14]. On the other hand, the EDA reactions of certain π – acceptors have successfully been utilized in pharmaceutical analysis [15]. For these wide applications, extensive studies on CT- complexes of π - acceptors have been performed [16]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes (CTC_S) which absorb radiation in the visible region [17].

This chapter presents the studies of CT complex formed between picric acid (2, 4, 6-trinitro phenol, PiOH) and p-nitroaniline (PNA). Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene [18]. The bond between the donor and acceptor is formed by the interaction between the electron poor ring of the picric acid and electron rich ring of anthracene. The compound thus formed is often referred to as CT complexes [18]. The charge transfer complexes produced by the reaction between picric acid and some aniline derivatives were also investigated [19] by using FTIR spectroscopy. Picric acid also forms charge transfer complexes with piperidine [20] and phenylphrine [21]. It was proved that a proton transfer interaction takes place between PiOH (picric acid) and X -Ph- NH_2 (aromatic amines) leading to the formation of PiO^- and X- Ph – NH_3^+ ions. The normal π – π* electronic interaction takes place by transferring an electron from the aniline ring to the picric acid. The significance of the effects of complexation on spectra has led to the necessity of studies to quantify the PiOH/PNA interaction. The purpose of the present work is precisely to investigate this interaction. The concept of CT interaction also offers a platform for explaining the interaction between electronic subsystems of PiOH and PNA and hence widens the scope of the present

investigation on understanding the molecular interaction of PNA with π acceptor PiOH.

2.2. Chemistry of Picric acid

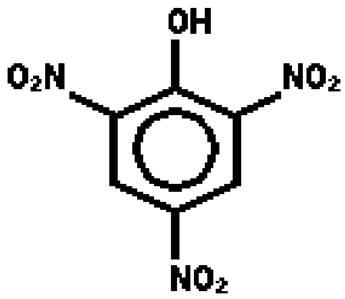
Picric acid is the chemical compound more formally called 2, 4, 6-trinitrophenol (TNP). This, is a yellow crystalline solid, is one of the most acidic phenols. Like other highly nitrated compounds such as TNT, picric acid is an explosive. Its name comes from Greek πικρος (*pik′ ros*), meaning "bitter", reflecting the bitter taste of picric acid.

2.2.1 History

Picric acid was probably first mentioned in the alchemical writings of Johann Rudolf Glauber in 1742. Initially, it was made by nitrating substances such as animal horn, silk, indigo, and natural resin. Its synthesis from phenol, and the correct determination of its formula, was successfully accomplished in 1841. Not until 1830 did chemists think to use picric acid as an explosive. Before then, chemists assumed that only the salts of picric acid were explosive, not the acid itself. In 1873 Hermann Sprengel proved it could be detonated and by 1894 the Russian workers had worked out a method of manufacture for artillery shells. Soon after, most military powers used picric acid as their primary high explosive material. However, shells filled with picric acid become highly unstable as the compound corrodes bomb casings to form metal picrates which are more sensitive than the parent phenol. The sensitivity of picric acid was demonstrated in the Halifax Explosion. Picric was used in the Second Boer War [22] and World War I, [23] but the 20th century saw picric acid largely replaced by TNT and cordite. Picric acid is also used in the analytical chemistry of metals, ores, and minerals.

In 1885, based on research of Hermann Sprengel, French chemist Eugène Turpin patented the use of pressed and cast picric acid in blasting charges and artillery shells. In 1887 the French government adopted it under the name melinite, with addition of gun cotton. Since 1888, Britain started manufacturing a very similar mixture in Lydd, Kent, under the name lyddite. Japan followed with an "improved" formula known as schimose. In 1889, a similar material, a mixture of ammonium cresylate with trinitrocresol, or an ammonium salt of trinitrocresol, started to be manufactured under the name ecrasite.

Picric acid



Picric acid	
Other names	Carbazotic Acid; phenol trinitrate; picronitric acid; trinitrophenol; 2,4,6-trinitro-1-phenol; 2-hydroxy-1,3,5-trinitrobenzene; TNP
Properties	
Molecular formula	$C_6H_3N_3O_7$
Molar mass	229.10 g/mol
Appearance	Colorless to yellow solid
Density	1.763 g/cm³, solid
Melting point	122.5 °C
Boiling point	> 300 °C (Explodes)
Solubility in water	1.40 g/100 mL
Acidity (pK_a)	0.38
Explosive data	
Explosive velocity	7,350 m/s at ρ 1.70

2.2.2 Synthesis

The aromatic ring of phenol is highly activated towards electrophilic reactions, and attempted nitration of phenol, even with dilute nitric acid, results in the formation of high molecular weight tars. In order to minimize these side reactions, anhydrous phenol is sulphonated with oleum, and the resulting p-phenolsulfonic acid is then nitrated with concentrated nitric acid. During this reaction, nitro groups are introduced, and sulfonic acid groups are displaced. The reaction is highly exothermic, and careful temperature control is required.

2.2.3 Uses

By far the largest use has been in munitions and explosives, as discussed above.In microscopy, picric acid is a reagent for staining samples, e.g., Gram staining. It has found some use in organic chemistry for the preparation of crystalline salts of organic bases (picrates) for the purpose of identification and characterization.

Bouin's picro-formol is a preservative solution used for biological specimens. Workplace drug testing utilizes picric acid for the Jaffe Reaction to test for creatinine. It forms a colored complex that can be measured using spectroscopy. Much less commonly, wet picric acid has been used as a skin dye or temporary branding agent. It reacts with proteins in the skin to give a dark brown color that may last as long as a month. In the early 20th century, picric acid was stocked in pharmacies as an antiseptic and as a treatment for burns, malaria, herpes, and smallpox.

2.2.4 Safety

Modern safety precautions recommend storing picric acid wet. Dry picric acid is relatively sensitive to shock and friction, so laboratories that use it store it in bottles under a layer of water, rendering it safe. Glass or plastic bottles are required, as picric acid can easily form metal picrate salts that are even more sensitive and hazardous than the acid itself. Industrially, picric acid is especially hazardous

because it is volatile and slowly sublimes even at room temperature. Over time, the buildup of picrates on exposed metal surfaces can constitute a grave hazard.

2.3. Chemistry of p- nitro aniline

4-Nitroaniline, p-nitroaniline or 1-amino-4-nitrobenzene is an organic compound with the formula $C_6H_6N_2O_2$. It is an organic chemical compound, consisting of a phenyl group attached to an amino group which is para to a nitro group. The chemical structure of p-nitroaniline is shown at the right. This chemical is commonly used as an intermediate in the synthesis of dyes, antioxidants, pharmaceuticals and gasoline, in gum inhibitors, poultry medicines, and as a corrosion inhibitor.

2.3.1 Synthesis

Below is an example synthesis of p-nitroaniline from aniline. The key step in this reaction sequence is an electrophilic aromatic substitution to install the nitro group *para* to the amino group. After this reaction, a separation must be performed to remove 2-nitroaniline, which is also formed in a small amount during the reaction [24].

2.3.2 Applications

4-Nitroaniline is a starting material for the synthesis of Para Red, the first Azo dye [25].

2.3.3 Toxicity

The compound is toxic by way of inhalation, ingestion, and absorption, and should be handled with care. Its LD50 in rats is 750 mg/kg when administered orally. p-nitroaniline is particularly harmful to all aquatic organisms, and can cause long-term damage to the environment if released as a pollutant.

p-nitroaniline

p-Nitroaniline	
Other names	4-nitroaniline 1-amino-4-nitrobenzene p-nitrophenylamine
Properties	
Molecular formula	$C_6H_6N_2O_2$
Molar mass	138.12 g/mol
Appearance	yellow or brown powder
Density	1.437 g/ml, solid
Melting point	146-149 °C (lit.)
Boiling point	332 °C
Solubility in water	<0.1 mg/ml at 21°C
Flash point	199 °C

2.4. Experimental

2.4.1 Materials and Methods

p-nitroaniline (CDH), picric acid (Aldrich) were obtained commercially and used without further purification. Acetone (Merck), ethanol (Merck analytical grade), and methanol (Merck) were redistilled prior to their uses.

2.4.2 Preparation of Standard Solutions

Solutions of donor at different concentrations, 1 $\times 10^{-2}$ M, 1.5 $\times 10^{-2}$ M, 2 $\times 10^{-2}$ M, 2.5 $\times 10^{-2}$ M and 3 $\times 10^{-2}$ M were prepared in different volumetric flask by dissolving PNA (p-nitroaniline) accurately weighted amount in acetone, ethanol and methanol . A dark yellow colored solution is obtained in all the three solvents.

A standard solution of acceptor 1 $\times 10^{-2}$ M concentration was prepared by dissolving weighted amount of picric acid in three solvents viz – acetone, ethanol, and methanol in different volumetric flask.

2.4.3 Synthesis of CT complex

Picric acid, (solid) was mixed with p- nitroaniline, (solid) in agate mortar in the stoichiometric ratio 1:1.The start of the reaction was indicated by a color change (orange- red). The mixture was thoroughly mixed and kept in oven below their mp. For a week, it was occasionally mixed during this period .The reaction product was washed several times with benzene to remove untreated components. The color of the final product was orange- red. The product was dried and kept in a desiccator.

2.4.4 Reaction product from solution

The saturated solution of picric acid and p-nitroaniline in acetone were mixed and crystallized from benzene. The solution was kept at room temperature for 16 days, giving, orange – red colored crystals.

2.4.5 Solid state reaction in capillary (reactants in contact)

A Pyrex glass capillary having an inner diameter of (0.186 cm) and length of about 5 cm was used for this purpose. One end of the capillary was sealed, and half of the capillary was filled with p-nitroaniline of particular size below 100 meshes. For uniform packing, each capillary was tapped for 5 min. the surface was smoothened with the help of a thin glass rod. The remaining half of the capillary was filled with picric acid (particle size < 100 mesh) in such a way that the two components came in close contact. After filling the capillary, the other end was also

sealed and kept in oven below their mp. At the junction of the two components, the reaction started with a color change (orange – red), and grew towards the side of picric acid.

FT-IR spectra of picric acid, p-nitroaniline 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.

2.4.6 Spectral measurements and determination of association constant

A 3ml volume of donor and acceptor were scanned separately through a UV-Vis spectrophotometer ELICO SL 177 at their wavelength of maximum absorptions which were 385 nm for picric acid, and 420 nm for p-nitroaniline shown in Fig 1. When 10 ml of acceptor solution and 10 ml volume of donor solution were mixed, a yellow colored charge transfer complex was formed. The wave length of maximum absorption of the resulting solution was determined from the Spectrophotometer. The mixture for each reaction was allowed to stand for 1day at room temperature to form stable complexes before analysis at the maximum absorbance. The concentration of picric acid was kept constant while that of donor were varied for each set of measurements.

Stoichiometry and association constant of the complex were determined by Benesi - Hildebrand equation [26] for cells with 1 cm optical path length

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

where $[A]_o$ and $[D]_o$ are the initial concentrations of the acceptor and donor respectively.

A = absorbance

K_{CT} = formation constant of the complex

ε_{CT} = molar absorptivity of the complex

eq. (1) is valid [26] under the condition $[D]_o >> [A]_o$ for 1:1 donor –acceptor complexes. In all cases linear plots according to eq. (1) were obtained. A plot $[A]_o/A$ versus $1/[D]_o$ to give a straight line with the slope $1/K_{CT}\varepsilon_{CT}$ and intercept $1/\varepsilon_{CT}$ the values of K_{CT} and ε_{CT} may be determined.

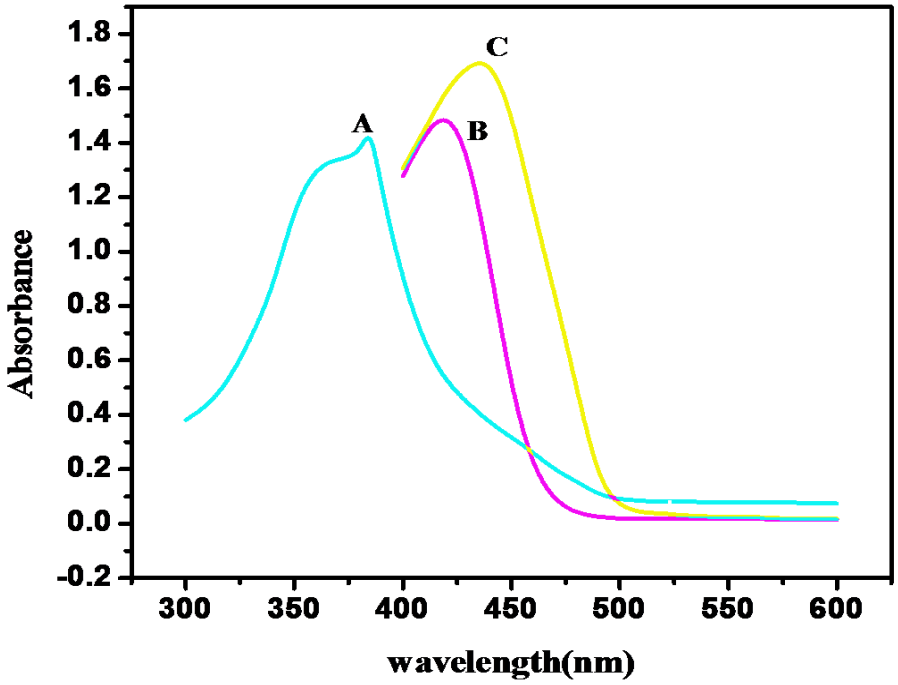


Fig. 1. Absorption spectra of (A) picric acid .01 M (B) p- nitroaniline .01 M (C) CTC of PNA .01 M and PiOH .01 M in acetone.

2.5. Results and Discussion

2.5.1 Observation of CT bands

The electronic absorption spectra of the donor p-nitroaniline, acceptor picric acid and the resulting complex in acetone, ethanol and methanol were recorded in the visible range 400 nm − 600 nm are shown in Figures (2, 3 & 4).

A 3 ml volume of donor and acceptor were scanned separately through a spectrophotometric titration at room temperature for the reaction mixture of donor (10 ml) and acceptor (10 ml) in different solvents viz. acetone, ethanol and methanol. A dark yellow color charge transfer complex was formed (The complex for each of the reaction mixture stood overnight at room temperature to form stable couple before analysis at the maximum absorbance 440 nm for acetone, 445 nm for ethanol and 450 nm for methanol.)

To obtain the CT bands, the spectrum of solution of 0.01 M PiOH (picric acid) and 0.01 M PNA in different solvents were recorded, 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. The CT absorption spectra were analyses 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 ($h\nu_{CT}$) are summarized in Table 2.

2.5.2 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

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

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

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

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 PNA are given in Table 2.

Briegleb and Czekalla [27] theoretically derived the relation

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

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.

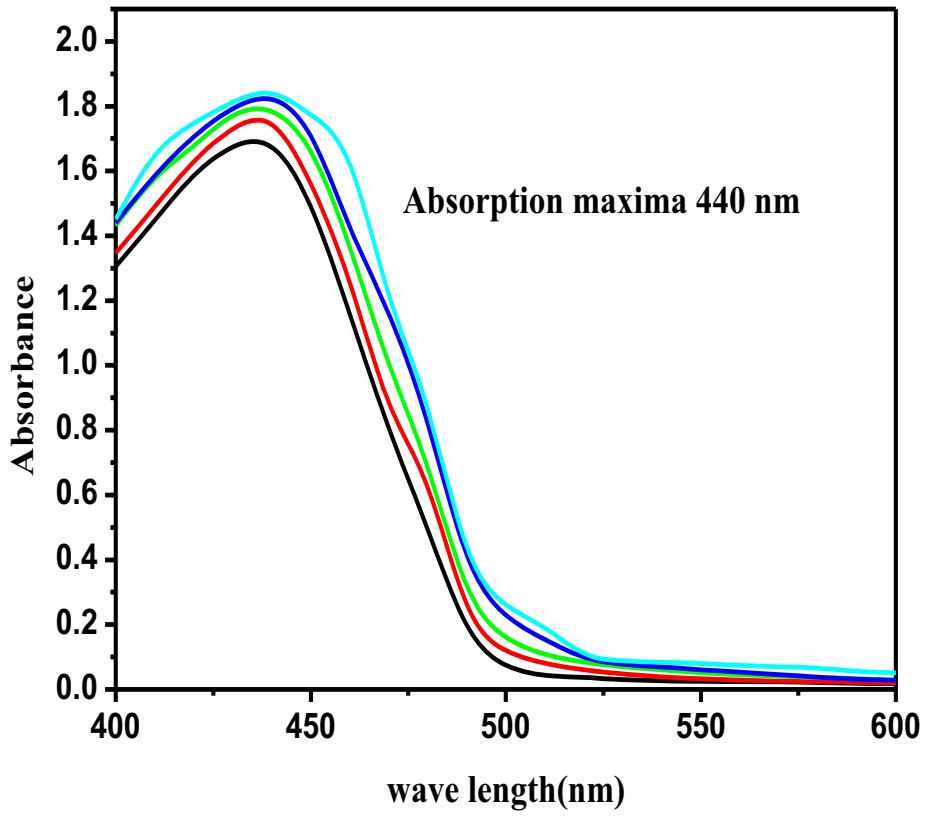


Fig.2. Absorption spectra of picric acid .01 M in acetone with addition of p-nitroaniline concentrations ranging from .01 M to .03 M are shown with increasing concentrations bottom to top.

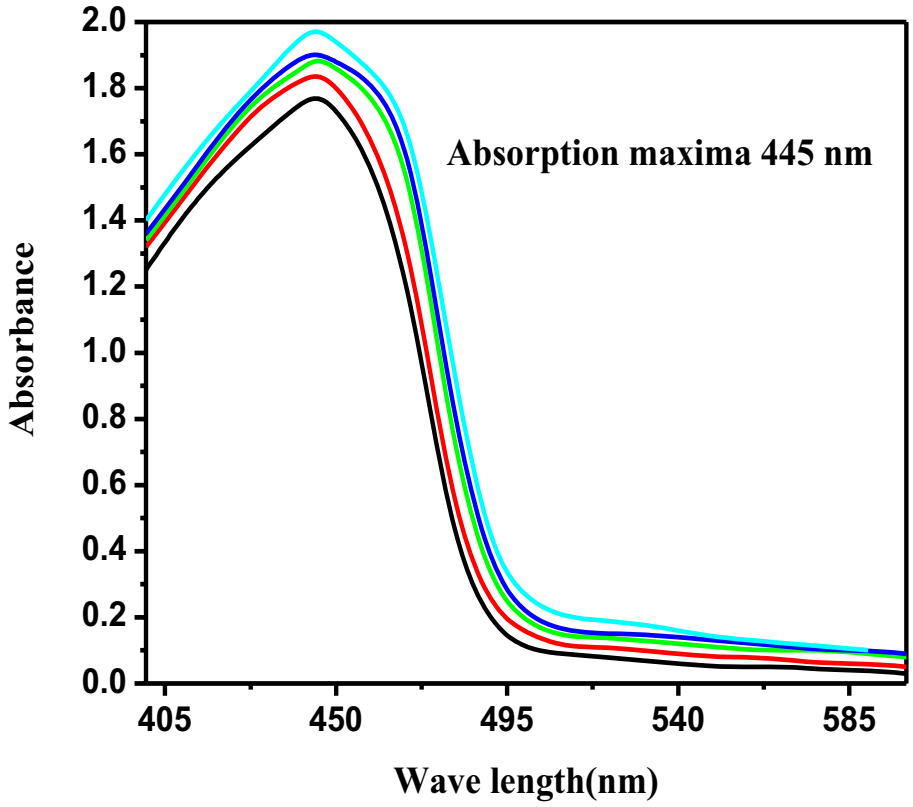


Fig. 3. Absorption spectra of picric acid .01 M in ethanol with addition of p-nitroaniline concentrations ranging from .01 M to .03 M are shown with increasing concentrations bottom to top.

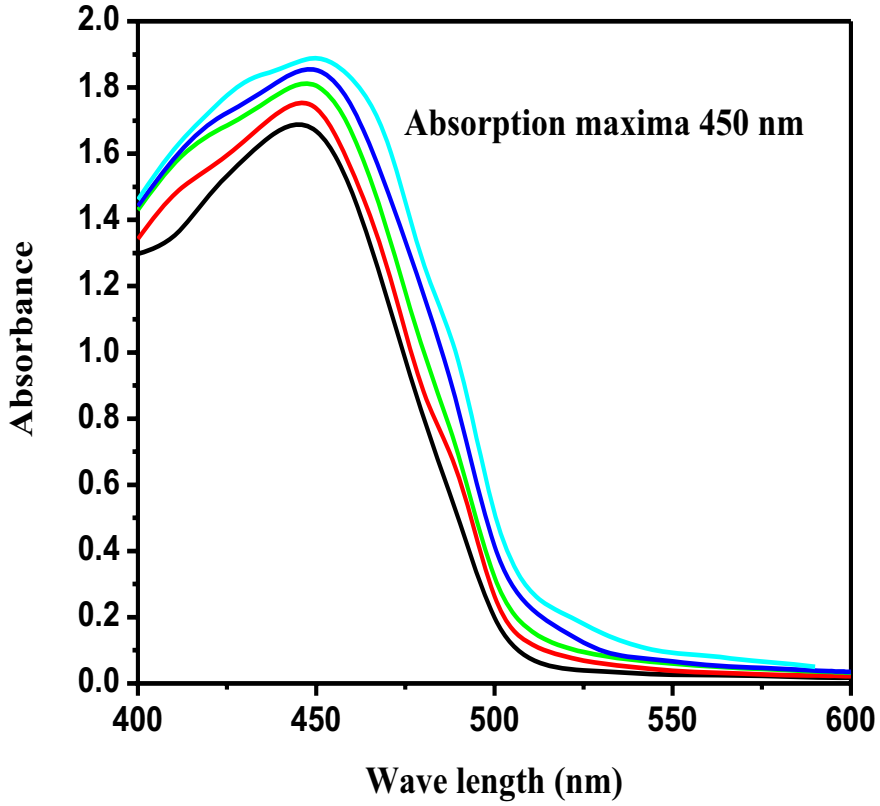


Fig. 4. Absorption spectra of picric acid .01 M in methanol with addition of p-nitroaniline concentrations ranging from .01 M to .03 M are shown with increasing concentrations bottom to top.

Table 1 Gaussian curve analysis for the CT in spectrum of PiOH with PNA different Polar solvents.

Systems	Area of the curve (A)	Width of the curve (W)	Centre of the curve (x_c)	Y_0
PiOH+PNA (Acetone)	141.99 ± 5.48	64.25 ± 2.44	429 ± 0.99	0.00228 ± 0 .022
PiOH+ PNA (Ethanol)	145.86 ±10.00	63.42 ± 4.05	434.13 ± 1.60	0.0192 ± 0.045
PiOH+ PNA (Methanol)	158.22 ± 9.13	71.74 ± 3.87	435 ± 1.506	- 0.0107 ± 0.037

Table 2 CT absorption maxima (λ_{CT}), transition energies ($h\nu_{CT}$) of PiOH complexes, experimentally determined ionization potential of the donor, oscillator strength (*f*), transition dipole strengths (μ_{EN}) and resonance energy (R_N) of complexes of (PiOH + PNA) in different solvents.

Systems	λ_{CT} (nm)	$h\nu_{CT}$ (eV)	I_D (eV)	$f \times 10^5$	μ_{EN} (Debye)	R_N (eV)
PiOH+PNA (Acetone)	429	2.89	9.32	2.69	0.937	0.0072
PiOH+PNA (Ethanol)	434.13	2.86	9.27	2.78	0.958	0.0074
PiOH+PNA (Methanol)	435	2.85	9.26	3.13	0.955	0.0074

2.5.3 Determination of resonance energy (R_N)

Briegleb and Czekalla [27] theoretically derived the relation

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

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.

2.5.4 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 [28]

$$I_D \text{ (eV)} = 5.76 + 1.53 \times 10^{-4} \quad \nu_{CT} \quad (6)$$

where ν_{CT} is the wave number in cm^{-1}corresponding to the CT band formed between donor and acceptor (PiOH).

2.5.5 Determination of Standard free energy changes (ΔG^0) and energy (E_{CT}) of the π-π interaction between donor and acceptor*

The standard free energy changes of complexation (ΔG^0) were calculated from the association constants by the following equation derived by Martin, Swarbrick and Cammarata [29]

$$\Delta G^0 = -2.303 \text{ RT log } K_{CT} \quad (7)$$

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), T is the temperature in Kelvin degrees (273 + ^{0}C) and, K_{CT} is the association constant of the complexes (l mol-^{1}).

The energy (E_{CT}) of the $\pi - \pi^*$ interaction between donor (PNA), and acceptor, (PiOH), is calculated using the following equation derived by G. Briegleb and Z. Angew [30].

$$E_{CT} = \frac{1243.667}{\lambda_{CT} nm} \quad (8)$$

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

2.5.6 Spectrophotometric study of formation constants of the complex of PiOH with PNA in different polar solvents

Picric acid as a π-acceptor forms CT complexes with aromatic amines [31-33]. The broad CT- bands were observed in the visible region for all the system studied where neither the donor and nor the acceptor absorbed. Pure solvents were used as the reference for all the system. The concentration of donor was in large excess over that of acceptor for every measurement $C_D >> C_A$ and changed over a wide range of concentration from 0.01 M to 0.03 M, while concentration of the acceptor (picric acid) was kept constant at 0.01 M in each solvents. In the studies it was observed that pale yellow colored solutions of picric acid in the three solvents viz- acetone, ethanol and methanol were obtained and greenish – yellow, light yellow and orange-yellow colored solutions of PNA in the same three solvents were obtained. When 10 ml of acceptor solution and 10 ml volume of donor solution were mixed, a dark yellow colored charge transfer complex was formed in the same three solvents. The change of color is attributed to the formation of CT complexes between picric acid and p-nitroaniline.

The typical absorption spectra of picric acid .01 M, p-nitroaniline .01 M, and CTC of PNA .01 M and PiOH .01 M in acetone are shown in Fig 1. The spectra obtained for PiOH/PNA system in acetone displays main absorption band at 440 nm which is not characteristic of the absorption of any of the reactants. These bands are characteristics of an intermolecular charge transfer involving the overlap of the lowest unoccupied molecular orbital (LUMO) of the acceptor with the highest occupied molecular orbital (HOMO) of the donor. The p- nitroaniline molecule is relatively electron rich and picric acid is relatively electron poor compound, they tend to associate with one another in a weak interaction known as an electron – donor- acceptor (EDA) complexes. The new, low energy absorptions observed in solutions containing both a donor and an acceptor have been described by Mulliken [34] as charge transfer transitions involve the excitation of an electron on the donor to an empty orbital on acceptor. The typical absorption spectra of CT complex of PiOH and PNA in acetone, ethanol, and methanol, where in the concentration of PiOH was kept constant and the concentration of PNA was varied is shown in Figs. 2, 3 and 4. In all the system studied, the absorption spectra are of similar nature

except for the position of absorption maxima λ_{CT} of the complex, the λ_{CT} was found to appear on the longer wavelength side of visible region. The spectra obtained for PiOH/PNA system display λmax at 450 nm in methanol, 445 nm in ethanol and 440 nm for acetone.

Stoichiometry and formation constant of the complexes were determined by using eq. (1) [26] and by plotting a graph of $[A]_o/ [A]$ versus $1/ [D]_o$. A linear relationship was determined the slope $1/K_{CT}\varepsilon_{CT}$ and intercept $1/\varepsilon_{CT}$ found for every system shown in Figs 5, 6 and 7 eq.(1), is valid under the condition $[D]_o >> [A]_o$ for 1:1 donor –acceptor complexes.

Thus, the stoichiometry of the complex was found to be 1:1. The mean values of spectrophotometric determination of stoichiometry, absorption maxima (λ_{CT}) and association constant (K_{CT}), molar absorptivities (ε_{CT}) of CTC of PiOH and PNA in acetone, ethanol and methanol at 298 K are listed in Table 3. The experimental data show that the change in dielectric constant has little effect on the λ_{CT} of the complex. The observation in the Table 3 reveals that the molar extinction coefficient ε_{CT} of the complex in all the system to be almost constant. The high values of the association constants K_{CT} as evident in the Table 3 indicate the strength of the binding between PiOH with PNA and the greater stability of the resultant CT- complex.

2.5.7 Effect of solvents on the formation of CT- complex

The experimental results of CT interaction between PiOH with PNA in different solvents are shown in Table 3. The values of association constants (K) are 752 (l mol^{-1}) in acetone, 689 (l mol^{-1}) in ethanol, and 518 (l mol^{-1}) in methanol, and the values molar extinction coefficients (ε_{CT}) are 194 (l $mol^{-1}cm^{-1}$) in acetone, 203 (l $mol^{-1}cm^{-1}$) in ethanol, and 202 (l $mol^{-1}cm^{1}$) in methanol. Spectroscopic properties were markedly affected by the variation in solvent polarity in which measurements were carried out. It is generally expected that the association constant K_{CT} for a

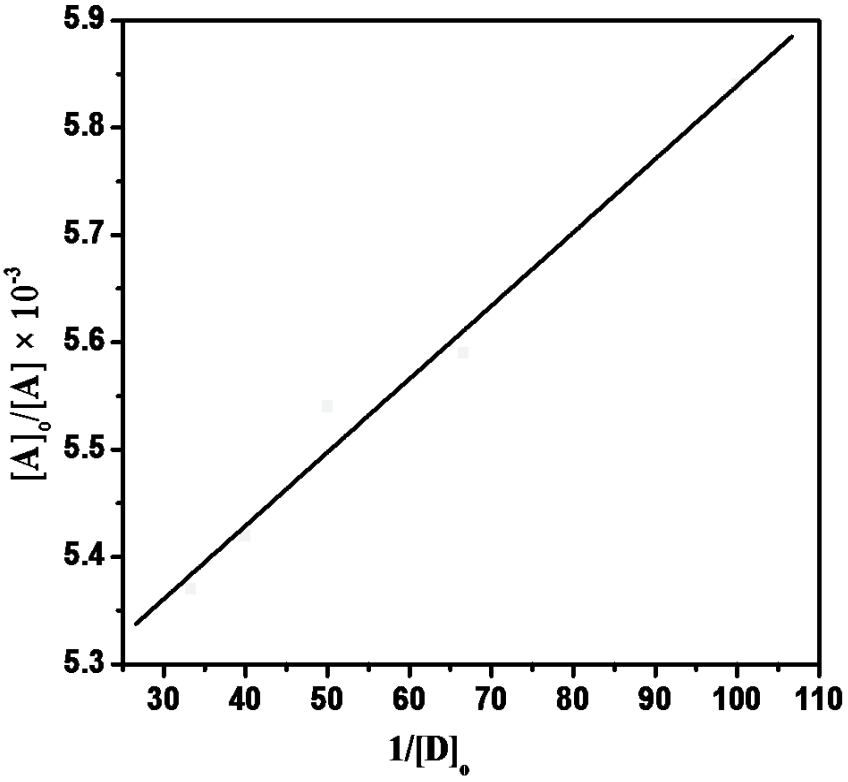


Fig. 5. Relation between $[A]_0$ / [A] and $1/[D]_0$ for CTC of PiOH/PNA in acetone.

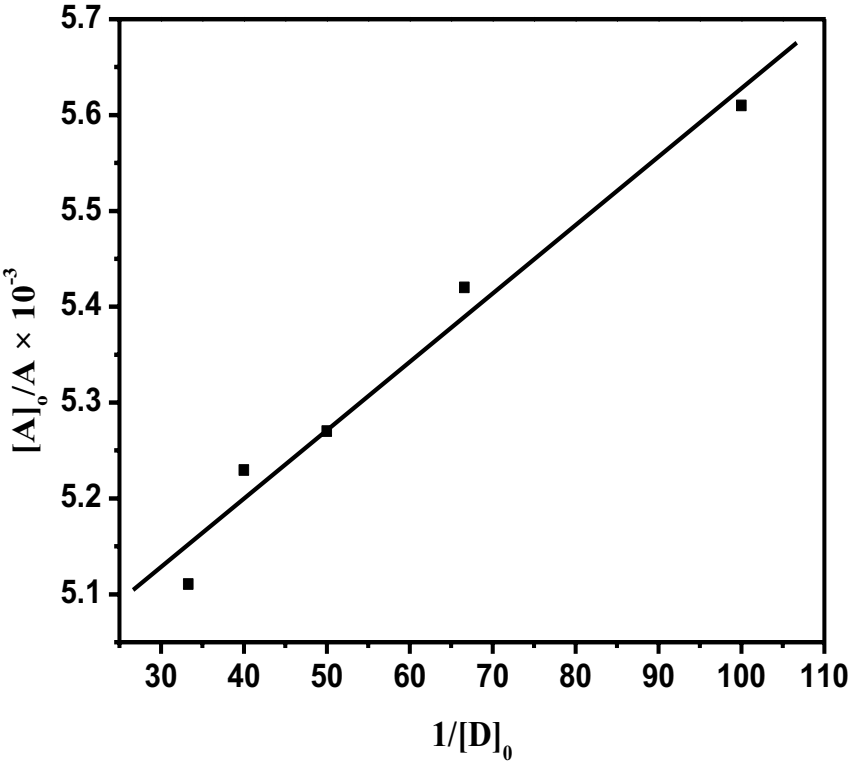


Fig. 6. Relation between $[A]_0 / A$ and $1/[D]_0$ for CTC of PiOH/PNA in ethanol.

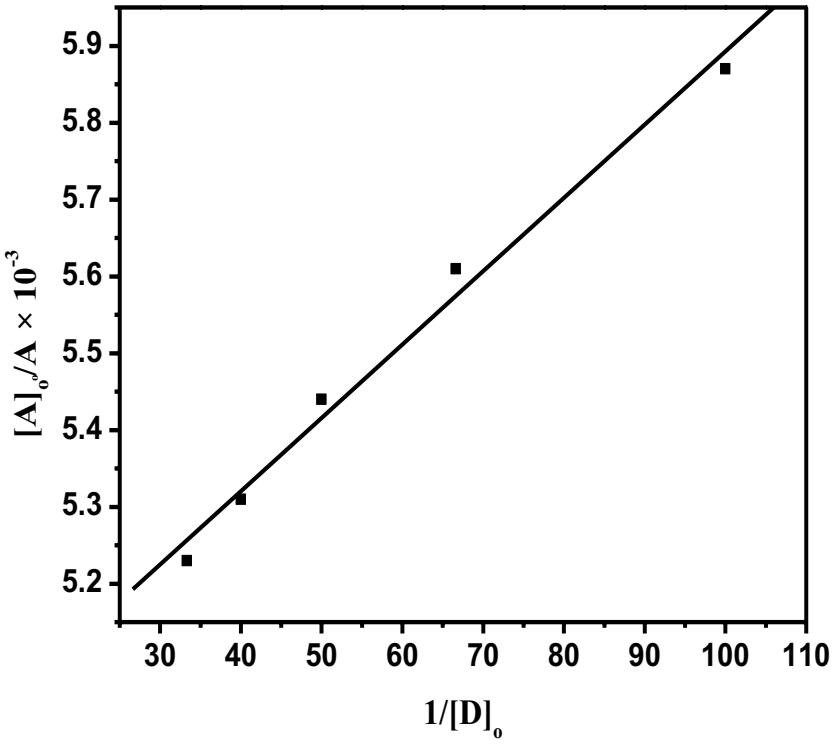


Fig. 7. Relation between $[A]_0 / A$ and $1/[D]_0$ for CTC of PiOH/PNA in methanol.

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 PNA in acetone, ethanol and methanol at 298 K

Systems	Temperature (K)	Donor concentration 1×10^{-2} M	$[A]_0$ 1×10^{-2} M	Absorbance at λ_{CT}(nm)	λ_{CT} (nm)	K_{CT} (l mol^{-1})	ε_{CT} (l mol^{-1} cm^{-1})
PiOH/PNA (Acetone)	298	1	1	1.710	440	752	194
		1.5		1.787			
		2		1.805			
		2.5		1.845			
		3		1.861			
PiOH/PNA (Ethanol)	298	1	1	1.780	445	689	203
		1.5		1.845			
		2		1.895			
		2.5		1.908			
		3		1.984			
PiOH/PNA (Methanol)	298	1	1	1.703	450	518	202
		1.5		1.780			
		2		1.837			
		2.5		1.880			
		3		1.909			

molecular complex formation will decrease or remain nearly the same as the medium changed from a non – polar to polar solvent. Such a situation prevails in a few CT systems for which both gas phase and solution data are available [35-37].

In the present investigation the K_{CT} value increases significantly from methanol to acetone with decreasing polarity of the solvent. Moreover, the increase in K_{CT} value with decreasing solvent polarity, may also be due to the fact that, CTC should be stabilized in a less polar solvent. Dissociation of the complex into D^+ and A^- radicals has been found to occur in the ground state [38]. It means that the CTC should be strong in less polar solvent than polar solvent. The red shift occurred in CTC complex was caused by a polarity change from using acetone to methanol. However the data reported in the present studies shows that PiOH interacts more strongly with PNA in acetone among the other two solvents.

The experimentally determined values of the oscillator strength, (f) are 2.69 $\times 10^{-5}$ in acetone, 2.78 $\times 10^{-5}$ in ethanol, and 3.13 $\times 10^{-5}$ in methanol, and the values of transition dipole moment (μ) are 0.937(Debye) in acetone, 0.958 (Debye) in ethanol, and 0.955 (Debye)in methanol. Values of resonance energy (R_N) are given in Table 2 and they are 0.0072 (eV) in acetone, 0.0074 (eV) in ethanol, and methanol. The data indicate that the complex should be stable in a less polar solvent (acetone) than the other two solvents (ethanol and methanol). The value of the molar extinction coefficient and oscillator strength increase with an increase in the dielectric constant of the solvent as reported in the earlier studies [39, 40]. The very low values of f, indicate that the CT complex studied here have almost neutral character in its ground state

2.5.8 Effect of solvents on the Standard free energy changes (ΔG^0) and ionization potentials (I_D) of donor

The ΔG^0 values of the complex were calculated from Gibbs, free energy of formation according to the eq. (7) given by Martin, Swarbrick and Cammarata [29].

$$\Delta G^0 = -2.303\ RT \log K_{CT} \qquad (7)$$

The parameters thus obtained are represented in Table 4 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 (PNA)

and acceptor (PiOH) is of exothermic in nature. The values of are ΔG^0 -16.410 ($kJmol^{-1}$) in acetone, -16.193 ($kJmol^{-1}$) in ethanol, and -15.485 ($kJmol^{-1}$) in methanol and they are also shown in Table 4. They are generally more negative as the association constants of the 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^0 become 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. (6) [28]. The calculated values of I_D are 9.23(eV) in acetone, 9.19 (eV) in ethanol and 9.15(eV) in methanol and they are shown in Table 5. The approximate consistency of I_D values, indicates that the ionization potential show a negligibly small effect on K_{CT} values.

2.5.9 Comparative study of IR spectra of CT complex and reactants

The FTIR spectra of the free acceptor and donor as well as the formed CT complex are given in Fig. 8 and their band assignments are reported in Table 6. However the appearance of a group of FTIR spectral bands in the spectra of CT complex support the conclusion that a deformation of the electronic environment of p- nitro aniline has occurred by accepting a proton from PiOH. The shift of the FTIR 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 [41].

The FTIR spectrum of the complex of PiOH and PNA in Fig. 8 shows the presence of characteristic absorption bands due to the varied forced constants in the donor and the acceptor species because of the prevalent charge transfer mechanism. This makes the crystals of this type more ionic than other organic crystals. In the FTIR spectra of the complex the O-H and N-H, stretching vibrations are observed at 3488.28 cm^{-1} and3390.14 cm^{-1} respectively. The band at 3106.05 cm^{-1} is due to the aromatic C-H stretching vibration. The $-NH_2$ deformation mode is observed by the absorption at 1633.96cm^{-1}. This band overlaps with the aromatic C = C stretching vibrations.

Table 4 Association constant (K_{CT}), correlation coefficients (r) and standard free energy changes (ΔG^o) of PiOH/PNA complexes obtained from Benesi-Hildebrand plots

Systems	K_{CT} ($l\ mol^{-1}$)	$-\Delta G^o$(298K) ($kJmol^{-1}$)	r
PiOH/PNA (Acetone)	752	16.410	0.9906
PiOH/PNA (Ethanol)	689	16.193	0.9869
PiOH/PNA (Methanol)	518	15.485	0.9938

Table 5 The CTC transition energies (ε_{CT}), CTC Absorption maxima (λ_{CT}), and ionization potential (I_D) of donor of in different solvents

Systems	ε_{CT} (eV)	λ_{CT} (nm)	I_D (eV)
PiOH/PNA (Acetone)	2.826	440	9.23
PiOH/PNA (Ethanol)	2.794	445	9.19
PiOH/PNA (Methanol)	2.763	450	9.15

Table 6 Characteristic infrared frequencies (cm^{-1}) and tentative assignments of PiOH, PNA and their complex.

PiOH	PNA	Complex	Assignments
3108 s, br	3481sharp	3488ms	ν(O-H) ,H bonded
-	3363 br	3390ms	ν (N-H)
-	3224 ms	3106 br	ν (C-H)
2875 w	-		ν_s(C-H)
	2711w		ν_{as}(C-H)
1630 vs	1633 vs	1633ms	$\nu_{as}NO_2$ ν (C=N)
1529 br 1606 ms	1592vs	-	ν(C=C)
-	1559w	1530vs	δ def (N-H), $+NH_2$ ring breathing bands
-	1538w		
-	1469vs	1432ms	C-H deformation
1437ms	1447s	-	
-	1397w	1344ms	ν(C-C), νsNO_2
1341vs	1304 br	1308ms	ν(C-N)
1275vs	1186 ms	1278w	ν(C-O)
1154ms	1109vs	1148ms	(C-H) in plane bending
1083ms		1117ms	
		1086ms	ν_s C-NO_2
916ms	996ms	915ms	δrock , $+NH_2$
830w	842 sharp		
779sharp	760sharp	848ms	$CH_{2\ rock}$ skeletal vibrations
734ms	699ms	781w	C-H out of plane
703ms	632ms	730ms	bending
663w	534ms	625w	-NO_2 wagg vibration
546w	483ms	502w	δ(ONO),PA
521w	-	-	
419sharp	419sharp	404w	CNC deformation

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

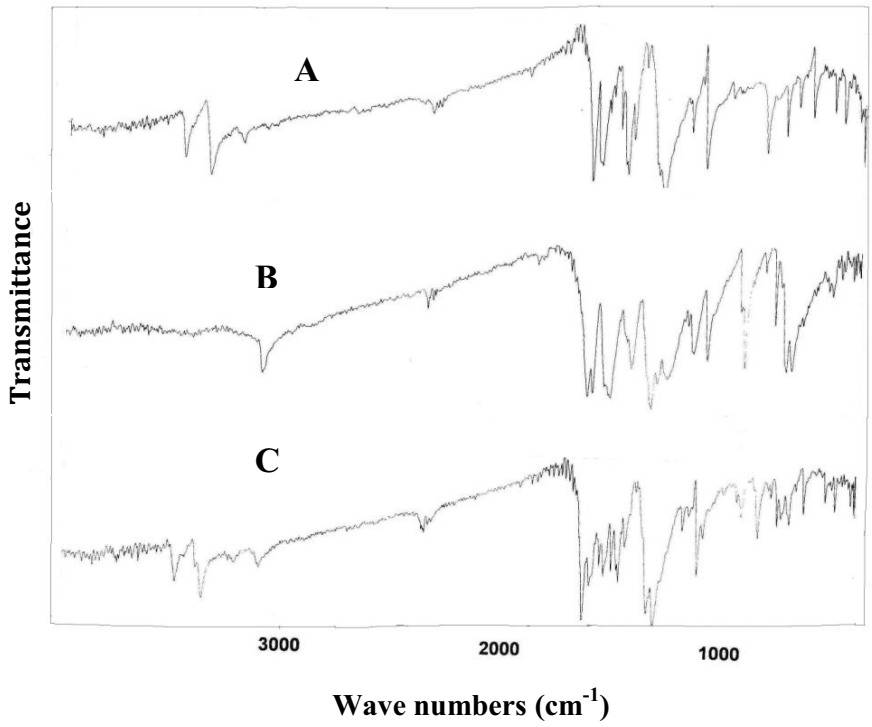


Fig.8. FTIR spectrum of (A) PNA donor (B) PA (acceptor) (C) complex.

The asymmetric and symmetric stretching vibrations of the $–NO_2$ group are observed at 1530.65 cm^{-1} and 1344.70 cm^{-1} respectively. Normally the asymmetric stretching vibration of in 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 (1530cm^{-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 [42]. The absorption at 1633.96cm^{-1}, 1530.65 $cm^{-1}$and 1432.51cm^{-1} are due to the aromatic C=C absorption stretching vibrations. The absorption at 1308.55$cm^{-1}$is due to the C-N stretching vibration. The C-O stretching vibration is observed as a band of medium intensity at 1148.42cm^{-1}. The C-H in plane bending vibration is observed at 1086.44 cm^{-1} and the C-H out of plane bending is shown by the presence of a band at 781.69 cm^{-1}. The C-NO_2 stretching is observed at 915.99 cm^{-1}. The NO_2 wagging vibrations are observed at 730.04cm-^{1} and 781.69cm^{-1}. The band at 702.816 cm^{-1} is due to the ring bending vibration. The assignments of various absorption frequencies of the compound are given in Table 6.

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- nitro aniline reveals that it forms 1:1 (A:D) complex in all the three solvents, viz -acetone, ethanol and methanol. In all the systems the stoichiometry is unaltered by changing the solvent. The association constants, K_{CT} and molar extinction coefficients, ε_{CT}, of all the 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 the CTC in more polar solvents and 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 the oscillator strengths (*f*) transition dipole moments (μ_{EN}) resonance energies (R_N) and standard free energies (ΔG^0) have been estimated for the PiOH/PNA systems in different polar 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 FTIR spectrum shows that the complex was formed by transferring a proton from the acceptor (PiOH) to the donor (PNA).

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