CHAPTER - 5

Spectrophotometric and Spectroscopic studies of charge transfer complexes of 1 – naphthylamine as an electron donor with Picric acid as an electron acceptor in different polar solvents.

5.1   Introduction

The study of Charge transfer interaction in solution between various electron donors with donor atoms like nitrogen, oxygen or sulfur and σ and π- electron acceptors have been the subject of many investigations [1-6]. A charge transfer phenomenon was first introduced by Mulliken [7]. Electron donor – acceptor (EDA) complexes are currently of great importance since these materials can be utilized as organic semiconductors [8], photo catalysts [9] and dendrimers [10]. They are also important in the redox processes [11]. There exists literature on theoretical [12-13] and experimental studies [14-23]. A vast number of the charge transfer complexes formed during the reaction of σ and π-acceptor with organic compound containing different sites of donation (nitrogen, oxygen or sulfur atoms) were extensively investigated [24-28].

In the present studies the CT complex formed between picric acid (acceptor) and 1-Naphthylamine (donor). Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene [29], some aniline derivatives [30] and also with aromatic amines [31-33]. 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-band structure stabilizing the complex [34].

In this work the study is focused on the interaction of PiOH (picric acid) with NPA (1-Naphthylamine) in solvents of different polarity at room temperature by visible spectra data of CT complex (π-π) of 1-Naphthylamine (donor) with π-acceptor, picric acid in different solvents viz.- acetone, ethanol, and methanol and also studied the effect of solvents on the formation of CT complex. The aim of the work is to determine the λ_{CT} reaction stoichiometry and formation constant as well as to investigate the nature and structure of the reaction product in both solution and solid and interpreting the nature of these interactions using ^{1}HNMR, FTIR spectra and electronic absorption.

5.2. Experimental

5.2.1 Materials and Methods

1-Naphthylamine (CDH), picric acid (Aldrich) were of the highest purity and used without further purification. Ethanol (Merck analytical grade), acetone (Merck), methanol (Merck) were used as received after checking their purity.

5.2.2 Preparation of standard solutions

Solutions of donor of different concentrations, 0.1M, 0.15M, 0.2M, 0.25M, and 0.3M were prepared in different volumetric flask by dissolving accurately weighed 1-Naphthylamine in different solvents such as acetone, ethanol and methanol.

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

5.2.3 Synthesis of CT complex

The solid CT complex of picric acid and 1- Naphthylamine was prepared by saturated solution of 1mmol of the donor in chloroform with saturated solution of 1mmol of acceptor. Upon addition, the mixture was stirred at the room temperature for half an hour producing precipitate. The complex was filtered off, washed with chloroform (5 ml) several time, and dried under vacuum.

5.3. Results   and   Discussion

5.3.1 Observation of CT bands

The electronic absorption spectra of the donor 1-Naphthylamine, acceptor picric acid and the resulting complex in 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 3ml volume of donor and acceptor were scanned separately through a spectrophotometric titration[35] at room temperature with their wavelength of maximum absorption 380nm for picric acid, 420nm for 1-Naphthylamine in acetone and for blank solvent(acetone) 320nm shown in Fig. 1. For the reaction mixture of donor (10ml) and acceptor (10ml) 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 standing overnight at room temperature to form stable complex before analysis at the maximum absorbance 445nm for acetone and methanol 450nm for ethanol. The concentration of the donor in the reaction mixture was kept greater than acceptor, $[D_0] \gg [A_o]$ [36, 37] and changed over a wide range from 0.1M to 0.3M while concentration of π- acceptor(picric acid) was kept fixed[36] at 0.01M in each solvents. These produced solutions with donor: acceptor molar ratios varying from 10:1 to 30:1, these concentrations ratios were used to straight line diagram for determination of the formation constants of CTC.

The spectrum of solution of 0.01M PiOH, and 0.1 M NPA in different solvents were recorded with solvents used as a reference, the longest wavelength peak was considered as CT peak[38].The absorption intensity changed 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 which were above mentioned above and given in Figures. [2, 3 & 4]. In all system 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 (hv) are summarized in Table 2.
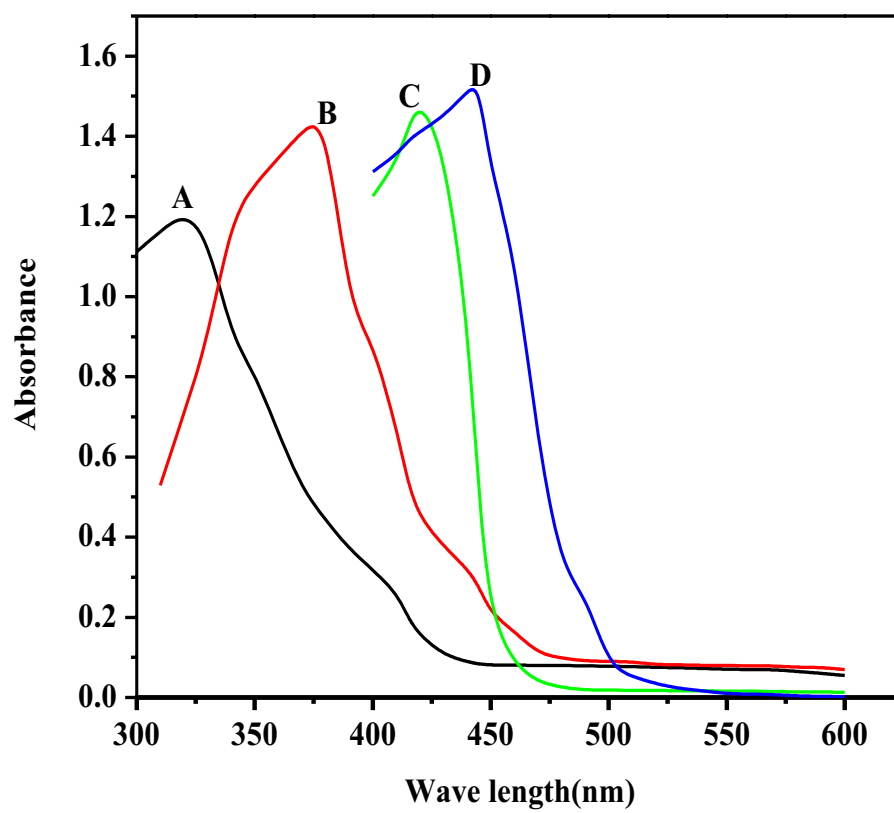
Fig. 1. Absorption spectra of (A) Blank solvent (acetone) (B) picric acid .01 M (C) 1-Naphthylamine .1 M (D) CTC of NPA .1M and PiOH .01M in acetone.
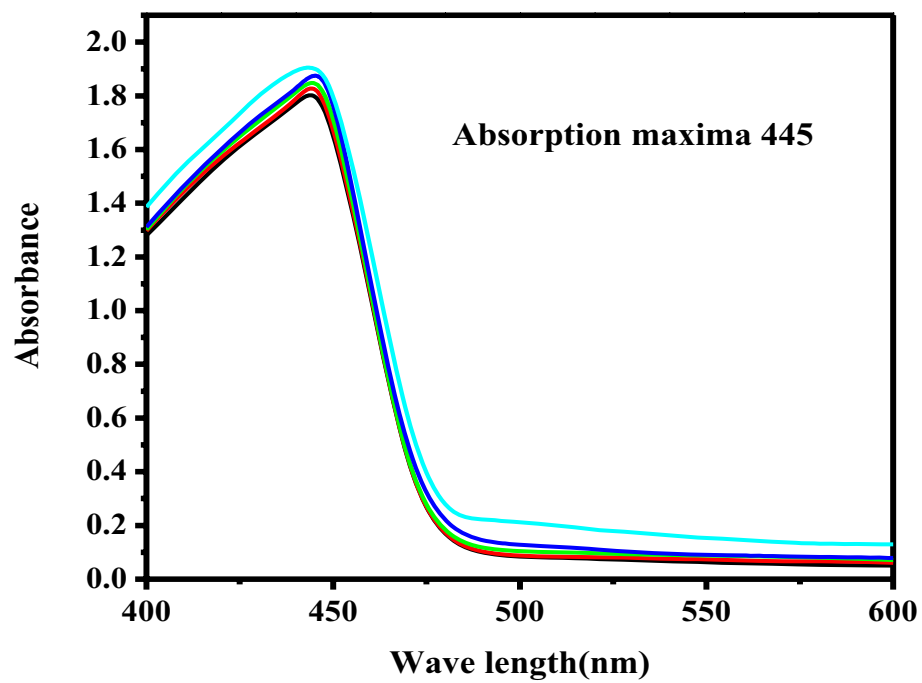
Fig. 2. Absorption spectra of picric acid (1×10^{-2}M) in acetone with addition of 1-Naphthylamine concentrations ranging 0.1M to 0.3M are shown with increasing concentrations bottom to top.
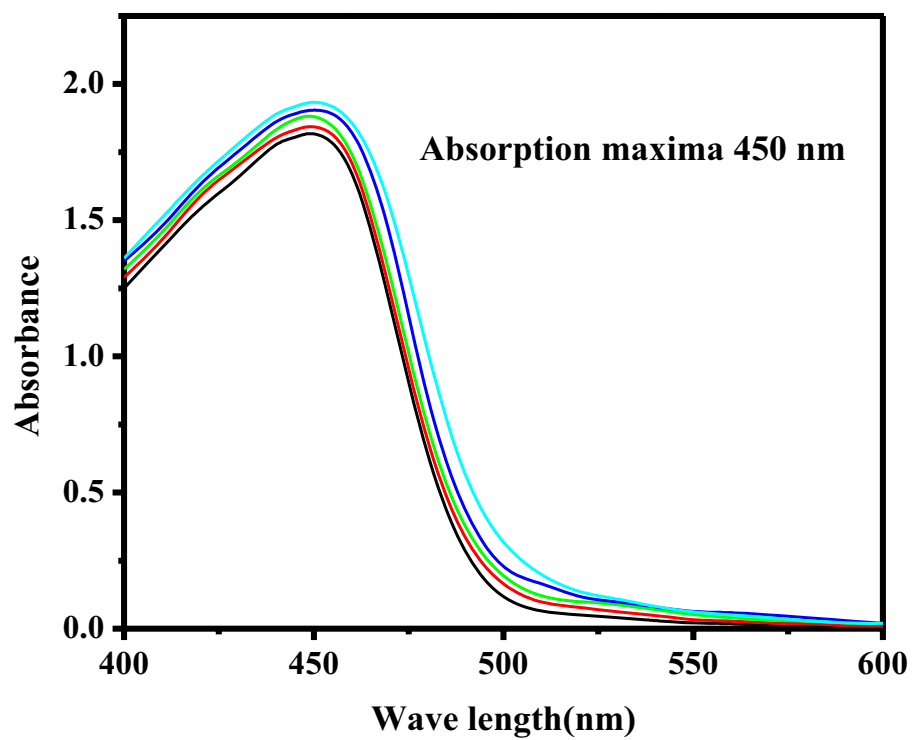
Fig. 3. Absorption spectra of picric acid (1×10^{-2}M) in ethanol with addition of 1-Naphthylamine concentrations ranging 0.1M to 0.3M are shown with increasing concentrations bottom to top.
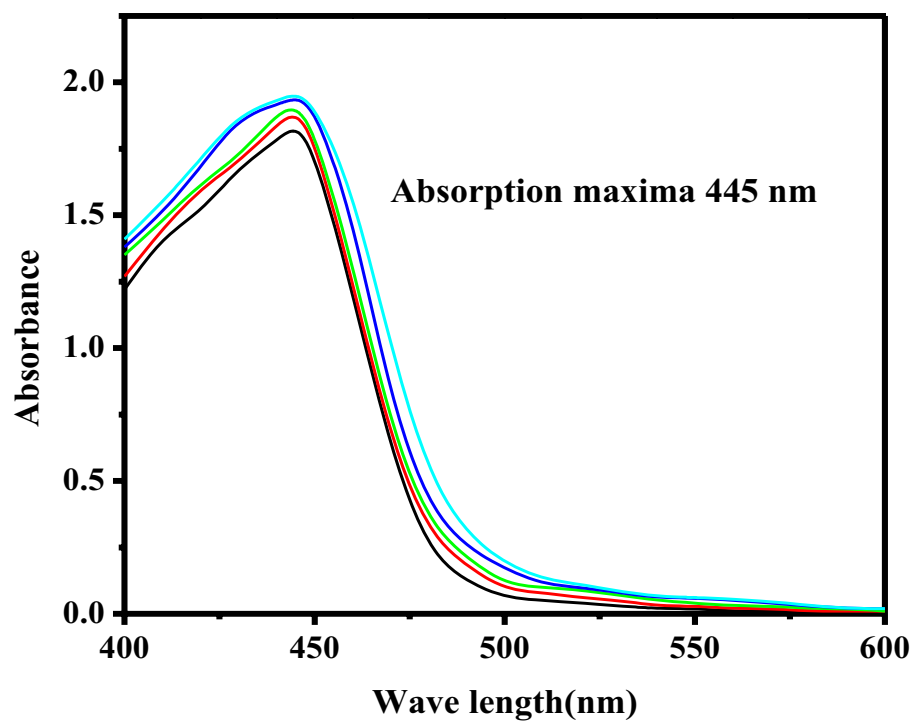
Fig. 4. Absorption spectra of picric acid (1×10^{-2}M) in methanol with addition of 1-Naphthylamine concentrations ranging 0.1M to 0.3M are shown with increasing concentrations bottom to top.

5.3.2 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 [39]

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

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

5.3.3 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

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT} \ d\nu \tag{2}$$

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

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

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

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

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 NPA are given in Table 2.

Table 1 Gaussion curve analysis for the CTC in spectram of PiOH with NPA in different polar solvents.

Systems	Solvents	A	W	X_c	Y_0
PiOH+NPA	acetone	123.25±9.10	53.05 ± 3.91	429.97±1.52	0.0382 ± 0.0460
PiOH+NPA	ethanol	154.94±10.63	64.88±4.075	435.89±1.61	-0.0135 ± 0.0479
PiOH+NPA	methanol	132.50 ± 8.17	56.27 ±3.37	431.66±1.33	-0.00168 ± 0.0399

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	Solvents	λ_{CT} (nm)	$h\nu_{CT}$ (eV)	I_D (eV)	$f \times 10^5$	μ_{EN} (Debye)	R_N (eV)
PiOH+NPA	acetone	429.97	2.89	9.30	2.22	0.936	0.0072
PiOH+NPA	ethanol	435.89	2.85	9.26	2.77	0.946	0.0072
PiOH+NPA	methanol	431.66	2.88	9.29	2.45	0.955	0.0074

5.3.4 Determination of resonance energy (R_N)

Briegleb and Czekalla [40] 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.

5.3.5 Determination of Standard free energy changes (ΔG°) and energy (E_CT) of the π-π* interaction between donor and acceptor

The standard free energy changes of complexation (ΔG°) were calculated from the association constants by the following equation derived by Martin, Swarbrick and Cammarata [41].

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

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), 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 $\pi -\pi^*$ interaction between donor (NPA), and acceptor, (PiOH), is calculated using the following equation derived by G. Briegleb and Z. Angew [42].

The calculated values of E_{CT} given in Table 5.

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

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

5.3.6 Spectrophotometric study of formation constants of the charge transfer complexes of PiOH/NPA in different polar solvents

Stoichiometries and the formation constants of the charge transfer complex of 1-Naphthylamine with picric acid have been determined in different polar solvents viz- acetone, ethanol and methanol at room temperature using Benesi–Hildebrand equation [43, 44]. 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 NPA to a solution of PiOH of fixed concentration follow the Benesi- Hildebrand [43, 44] equation in the form.

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

where $[D]_o$ and $[A]_o$ are the concentrations of the 1-Naphthylamine 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) [43, 44] is valid under the condition $[D]_o \gg [A]_o$ [36, 37] for 1:1 donor-acceptor complexes. The concentration of the donor (NPA) was changed over a wide range from 0.1M to 0.3M while concentration of π acceptor PiOH was kept fixed at 0.01M in each reaction mixture. These produced solution with donor: acceptor molar ratio varying from 10:1 to 30:1, experimental data are given in Table 3.

The Benesi – Hildebrand [43, 44] method is an approximation that has been used many times and giving 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 increasing polarity and addition of NPA. The typical absorbance data for charge transfer complexes of NPA with PiOH in different polar solvents at room temperature are reported in Table 1 & 3. In all systems very good linear plots according to eq. (7) [43, 44] are obtained, shown in Fig 5. Formation constants for the complex in different polar solvents at room

temperature determined from the BH plots are summarized in Table 3. The correlation coefficients of all such plots were above than 0.95. Plots of $[A]_0/A$ against $1/[D]_o$ were found to be linear in all systems in Fig. 5 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.
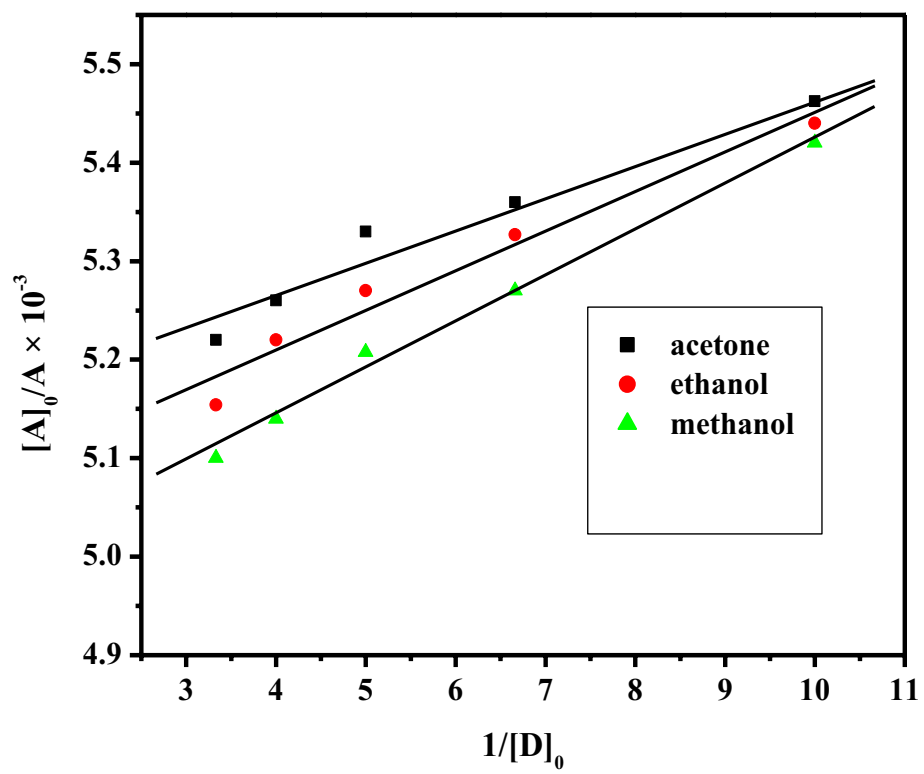
5.3.7   Effect of solvents on the formation of CT- complexes

The experimental results of the CT interaction between PiOH with NPA in different polar solvents show the values of association constants K_{CT} $157(1mol^{-1})$ in acetone, $117(1mol^{-1})$ in ethanol, and $107(1mol^{-1})$ in methanol and the values of molar extinction coefficient ε_{CT} $194(1mol^{-1}cm^{-1})$ in acetone,$198(1mol^{-1}cm^{-1})$ in ethanol, and $202(1mol^{-1}cm^{-1})$ 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 acetone 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 less polar solvent [7]. 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 less polar solvent than polar solvent. The red shift occurred in CTC complex caused by polarity change on going from acetone to methanol.

However the data given in Table 3 shows that PiOH interacts more strongly with NPA in acetone among the other two solvents. The experimentally determined values of oscillator strength (*f*) 2.22×10^{-5} in acetone, 2.77×10^{-5} in ethanol, and 2.45 $\times 10^{-5}$ in methanol, and the values of transition dipole moment (μ_{EN}) 0.936(Debyes) in acetone, 0.946 (Debyes) in ethanol, and 0.955 (Debyes)in methanol, and values of resonance energy [R_N] (eV) 0.0072 in methanol). The very low values of *f* indicate acetone, 0.0072 in ethanol, and 0.0074 methanol, given in Table 2 indicate that complex should be stable in less polar solvent (acetone) than other two solvents (ethanol and 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 NPA in acetone, ethanol, and methanol at 298 K

Systems	Solvents	Temperature (K)	Donor concentration in M	$[A]_0$ M	Absorbance at λ_{CT} (nm)	λ_{CT} (nm)	K_{CT} (lmol^{-1})	ε_{CT} (1mol^{-1} cm^{-1})
PiOH+NPA	acetone	298	0.1		1.832			
			0.15	0.01	1.863	445	157	194
			0.2		1.875			
			0.25		1.898			
			0.3		1.913			
PiOH+NPA	ethanol	298	0.1	0.01	1.835			
			0.15		1.857	450	117	198
			0.2		1.896			
			0.25		1.913			
			0.3		1.945			
PiOH+NPA	methanol	298	0.1					
			0.15	0.01	1.843			
			0.2		1.894	445	107	202
			0.25		1.915			
			0.3		1.945			
					1.960			

Fig. 5. Relation between $[A]_0/A$ and $1/[D]_0$ of PiOH +NPA in acetone, ethanol, methanol.

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 (NPA) and acceptor (PiOH) is of exothermic   in nature. The values of $\Delta G^{\,o}$, - 12.495 (kJmol^{-1}) in acetone, -11.754(kJmol^{-1}) in ethanol, and -11.525(kJmol^{-1}) in methanol given in Table 4 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 λCT of the CTC from eq. (1) [39]. The calculated values of I_D 9.19(eV) in acetone, 9.15(eV) in ethanol, and 9.19(eV) in methanol of PiOH/NPA system   are shown in Table 5. The approximate constancy of I_D values, indicates that the ionization potential show a negligibly small effect on K_{CT} values.

5.3.8   Comparative study of FTIR spectra of CT complex and reactants

FTIR spectrum of picric acid, 1-Naphthylamine and the reaction product obtained from solid state reaction between acceptor and donor were recorded with the help of FTIR spectrometer INTERSPEC–2020 (spectra lab U.K.) measured in KBr pellets. FTIR spectrum of the free acceptor and donor as well as the formed CT complex is given in Fig 6 and their bands assignments reported in Table 6.

The FTIR spectrum of picric acid shows a peak at 3104 cm^{-1} is due to υ_{OH} vibrations and the FTIR spectrum of 1-Naphthylamine show number of peaks at 3409-3043cm^{-1} are due to υ_{NH2} vibrations. As a result of complexation when picric acid reacted with 1-Naphthylamine, bands due to υ_{OH} and υ_{NH2} vibrations are broadened and shifted to lower wave number (3209-2591cm^{-1}) [46] see the FTIR spectrum of complex. In the FTIR spectrum of complex the broadened peaks occurred at 2845cm^{-1} and 2591cm^{-1} region are due to hydrogen bonding in the complex. The results show that the –OH group of picric acid is hydrogen bonded with the hydrogen atom of amino group of 1-Naphthylamine. Thus, one can say that a charge transfer molecular complex between picric acid and 1-Naphthylamine stabilized by hydrogen bonding.

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

Systems	Solvents	E_{CT} (eV)	λ_{CT} (nm)	I_D(eV)
PiOH+NPA	acetone	2.794	445	9.19
PiOH+NPA	ethanol	2.763	450	9.15
PiOH+NPA	methanol	2.794	445	9.19

Table5 The CTC transition energies (E_{CT}) CTC absorption maxima (λ_{CT}) and Ionization potential (I_D) of donor of in different polar solvents

Systems	Solvents	E_{CT} (eV)	λ_{CT} (nm)	I_D(eV)
PiOH+NPA	acetone	2.794	445	9.19
PiOH+NPA	ethanol	2.763	450	9.15
PiOH+NPA	methanol	2.794	445	9.19

5.3.9 ^{1}H NMR Spectrum of CT 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 7. 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.

The singlet peak at δ = 8.593 ppm 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 Naphthylamine molecule. The signal is split into triplet by two neighborhood proton one 8.571 ppm [47]. The triplet peaks at δ = 8.032 ppm is due to the C_1 carbon atom of 1-each on C_2 and C_3 carbon atom and the doublet peak 7.793 ppm are assigned to the proton on C_4, C_5 carbon atom of 1-Naphthyl amine moiety in the complex. The same were observed at in free 1-Naphthylamine. The multiple peak at 7.669 ppm are assigned to the proton on C_6, C_7, C_8, C_9 and C_{10} carbon atom of 1-Naphthyl amine and these peaks are also observed in free 1-Naphthylamine molecule. The peak are observed at 3.513 ppm in complex is due to the formation of hydrogen bonding (N^+–H—O^-) between picric acid and 1-Naphthylamine because in free picric acid the peak at δ =11.94 ppm is due to the –OH proton of picric acid [47] which are absent in spectrum on CT complex. This up field shift is due to the hydrogen bonding between –OH group of picric acid and -NH_2 group of 1-Naphthylamine. These shifts assume that the amino group and phenolic group are mainly involved in the formula of the CT complex. Mechanism and structure of the CT complex of acceptor and donor is given in scheme 1.

Table6 Characteristic infrared frequencies (cm^{-1}) and tentative assignments for PiOH, NPA and their complex.

PiOH	NPA	Complex	Assignments
3104 s, br	3409br	3209br	ν(O-H),PA
-	3338 br	3083 br	ν (N-H),NPA
-	3206br		ν_{as} (C-H),CH$_3$ + CH$_3$
2870w	3043 br	-	ν(C-H),aromatic ν ($^+$NH)
-		2845br	hydrogen bonding
		2591br	b/w –OH—H--NH
1633 vs	-		
1606ms	1623vs	1608ms	ν_{as}(NO$_2$), PA
1531 br	1572vs	1569ms	ν(C=C), aromatic
-	1510vs	1530ms	δ def (N-H), +NH$_2$ ring breathing bands
	1450S	1493vs	C-H deformation
1435ms	1406br	1417ms	
-	1373sh	1334br	ν(C-C), ν_sNO$_2$, PA
1343vs	-	-	ν_{as}(C-N)
1277vs	1287vs	1267br	ν(C-O)
1150ms	1170w	1165ms	
1089ms	1083br	1083ms	ν_s(C-N)
	1012sharp		
916ms	951sharp	936sharp	δ (C-H) in plane bending
830w	854sharp	915sharp	δrock , +NH$_2$
783sharp			CH$_2$ $_{rock}$ skeletal vibrations
	763vs	768vs	C-H out of plane
727ms	666vs	697ms	bending
663w	574ms	539sh	
544w	457ms	468br	δ(ONO), PiOH
521w	-	-	CNC deformation
419sharp	417sharp	412ms	

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
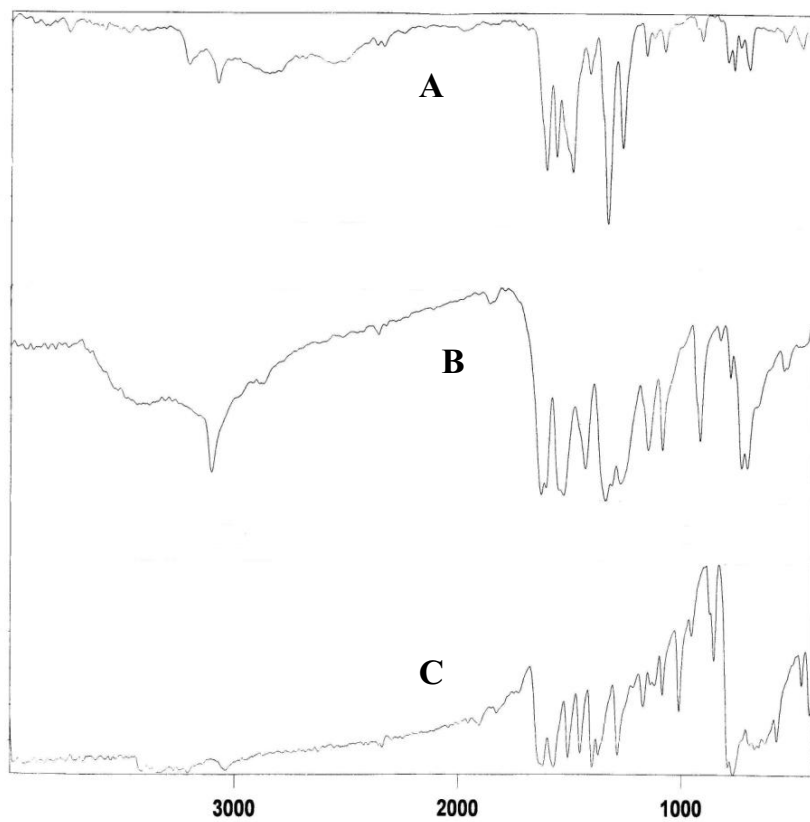
Fig. 6. FTIR spectrum of (A) Complex of NPA and PA (B) Acceptor PA(C) Donor NPA
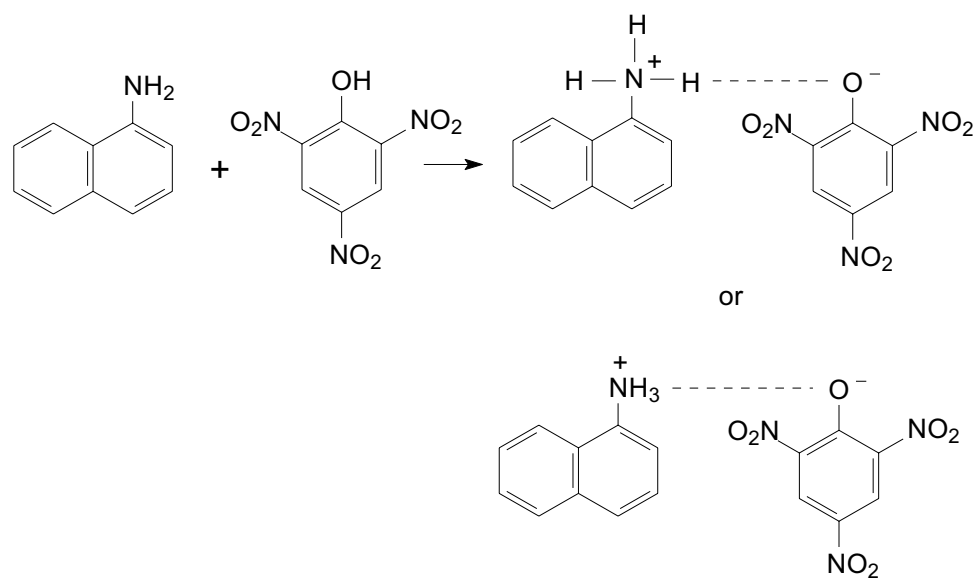
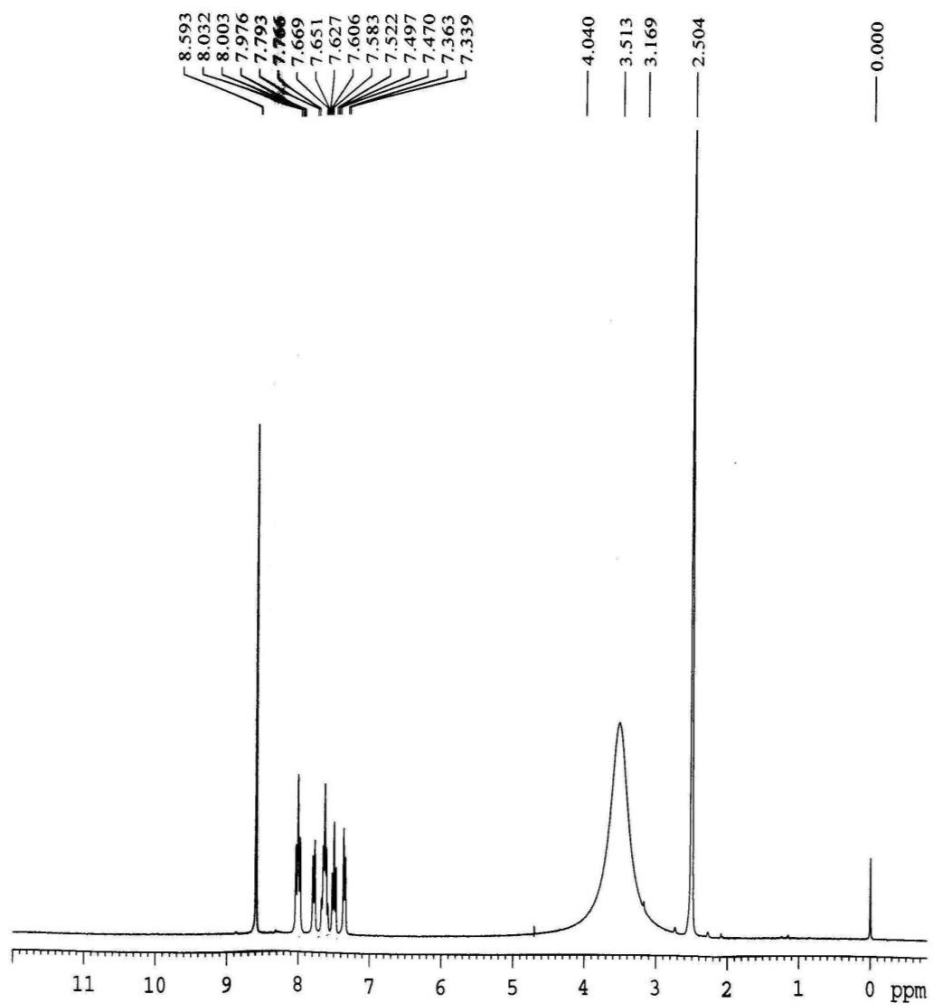**Scheme I** Mechanism for interaction between 1-Naphthylamine with picric acid

Fig. 7. ^{1}H NMR Spectrum of complex

Conclusions

The UV –Vis   spectrophotometric method for the study of CTC of picric acid with 1-Naphthylamine reveals that it forms 1:1 (A: D) complex in all three solvents, viz - 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 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/NPA 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 and NMR spectrum shows that the charge transfer molecular complex formed between NPA and PA stabilized by hydrogen bonding which is formed between –OH group of picric acid and hydrogen atom of amino group of 1-Naphthylamine.