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Spectrophotometric and spectroscopic studies of charge transfer complex of 1-Naphthylamine as an electron donor with picric acid as an electron acceptor in different polar solvents

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ABSTRACT

The charge transfer complex of 1-Naphthylamine as a donor with π-acceptor picric acid has been studied spectrophotometrically in different solvents at room temperature. The results indicate that the formation of charge transfer complex is high in less polar solvent. The stoichiometry of the complex was found to be 1:1 by straight line method. The data are analysed in terms of formation constant (K_{CT}), molar extinction coefficient (ε_{CT}), standard free energy (ΔG^o), oscillator strength (f), transition dipole moment (μ_{EN}), resonance energy (R_N) and ionization potential (I_D). It is concluded that the formation constant (K_{CT}) of the complex is found to be depends upon the nature of both electron acceptor and donor and also on the polarity of solvents. Further the charge transfer molecular complex between picric acid and 1-Naphthylamine is stabilized by hydrogen bonding.

1. Introduction

Charge transfer complexation is important phenomenon in biochemical and bioelectrochemical energy transfer process [1]. Charge transfer phenomenon was introduced first by Mulliken. The term charge transfer gives a certain type of complex resulting from interactions of donor and acceptor with the formation of weak bands [2,3] and discussed widely by Foster [4]. Molecular interactions between electron donors and acceptors are generally associated with the formation of intensely colored charge transfer complexes (CTC_S) in which absorb radiation in the visible region [5]. Molecular complexation and structural recognition are important processes in biological systems, for example, drug action, enzyme catalysis and ion transfers through lipophilic membranes all involve complexation [6]. Charge transfer complexes are currently of great importance since these materials can be utilized as organic semiconductors [7], photo catalysts [8] and dendrimers [9]. They are also important in studying redox processes [10], second order non-liner optical activity [11] and micro emulsion [12].

This paper describes the studies on the formation of CT complex formed between picric acid (acceptor) and 1-Naphthylamine (donor). Picric acid forms molecular complexes with aromatic hydrocarbons such as anthracene [13], some aniline derivatives [14] and also with aromatic amines [15–17]. Mulliken suggested that the formation of molecular complexes from two aromatic molecules can arises due to an electron transfer 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 [2].

This study deals with the interaction of PiOH (picric acid) with NPA (1-Naphthylamine) in solvents of different polarity at room temperature by using 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. The effect of solvents on the formation of CT complex was also studied with the aim to determine λ_{CT} reaction stoichiometry, formation constant. The nature and structure of the reaction product both in solution and solid phase has been studied to interpret the nature of interactions using ^{1}H NMR, FTIR spectra and electronic absorption.

2. Experimental

2.1. Materials and methods

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

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2.2. Preparation of standard solutions

Solutions of 1-Naphthylamine (donor) of different concentrations, 0.1 M, 0.15 M, 0.2 M, 0.25 M, and 0.3 M were prepared separately in different volumetric flasks in different solvents (acetone, ethanol, and methanol).

0.01 M standard solution of picric acid (acceptor) was prepared by dissolving in above solvents respectively.

The electronic absorption spectra of the donor 1-Naphthylamine, acceptor picric acid and the resulting complex in acetone, ethanol and methanol respectively were recorded in the visible range 400–600 nm using a spectrophotometer (ELICO SL 177 scanning mini spectrophotometer) with a quartz cell of 1 cm path length.

2.3. Synthesis of CT complex

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

FTIR spectrum of picric acid, 1-Naphthylamine, and the reaction product obtained from solid state reaction between acceptor and donor was recorded with the help of FTIR spectrometer INTERSPEC-2020 (spectra lab, UK) measured in KBr pellets.

The nuclear magnetic resonance, ^{1}H NMR spectrum of CT complex is measured in DMSO using Bruker Advance II 400 NMR spectrometer.

3. Results and discussion

3.1. Observation of CT bands

A 3 ml volume of donor and acceptor were scanned separately by spectrophotometric titration [18] at room temperature at their wavelength of maximum absorption, 380 nm for picric acid, 420 nm for 1-Naphthylamine in acetone and 320 nm for blank solvent (acetone) (Fig. 1). The reaction mixture of donor (10 ml) and acceptor (10 ml) in different solvents viz, acetone, ethanol and methanol formed a dark yellow colored charge transfer complex. The complex for each of the reaction mixture was kept overnight at room temperature to form a stable complex, before analysis at the maximum absorbance 445 nm for acetone and methanol and 450 nm for ethanol were recorded The concentration of the donor in the reaction mixture was kept greater than acceptor, $[D_o] \gg [A_o]$ [19,20] and changed over a wide range from a concentration 0.1–0.3 M. The concentration of π-acceptor (picric acid) was kept fixed [19] at 0.01 M in each solvent. These molar ratios (10:1–30:1) of donor:acceptor was used to draw a straight line diagram for determination of the formation constants of CT complex.

The electronic absorption spectra of 0.01 M PiOH, and 0.1 M NPA in different solvents were recorded and the longest wavelength peak was considered as CT peak [21]. The addition of the donor changed the absorption intensity to higher values. These measurements were based on the CT absorption bands exhibited by the spectra of the systems mentioned as above and are given in Figs. 2–4. In all systems studied the absorption spectra are of similar nature except for the position of absorption maxima (λ_{CT}) of the complex. The CT complex 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 the wavelength and absorbance, respectively. The results of the Gaussian analysis for all the systems under study are shown in Table 1. The wavelengths at these new absorption

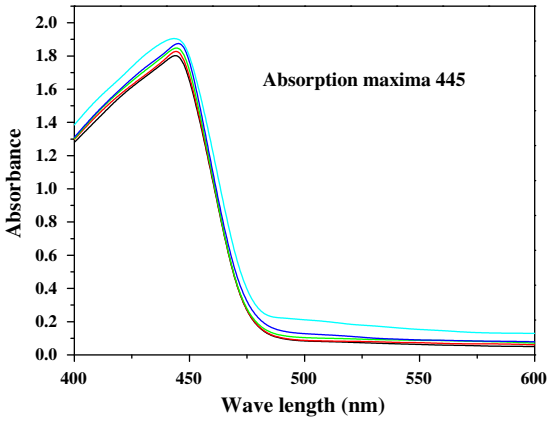


Fig. 2. Absorption spectra of picric acid (1×10^{-2} M) in acetone with addition of 1-Naphthylamine concentrations ranging from 0.1 M to 0.3 M are shown with increasing concentrations bottom to top.

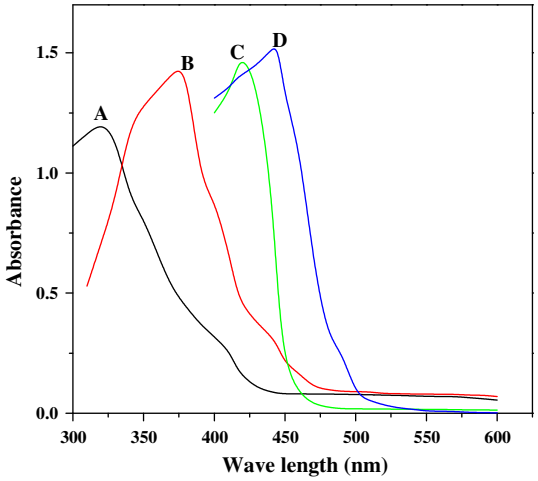


Fig. 1. Absorption spectra of: (A) blank solvent (acetone) (B) picric acid 0.01 M (C) 1-Naphthylamine 0.1 M (D) CTC of NPA 0.1 M and PiOH 0.01 M acetone.

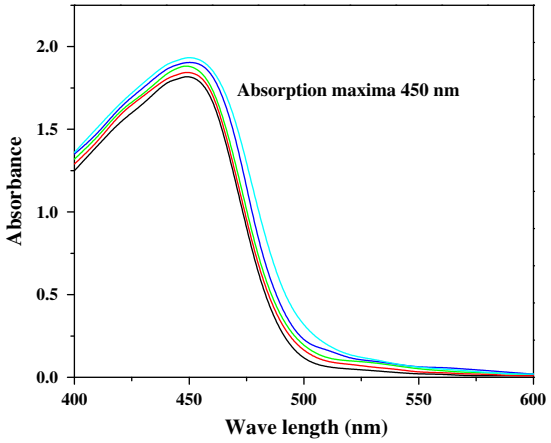


Fig. 3. Absorption spectra of picric acid (1×10^{-2} M) in ethanol with addition of 1-Naphthylamine concentrations ranging from 0.1 M to 0.3 M are shown with increasing concentrations bottom to top.

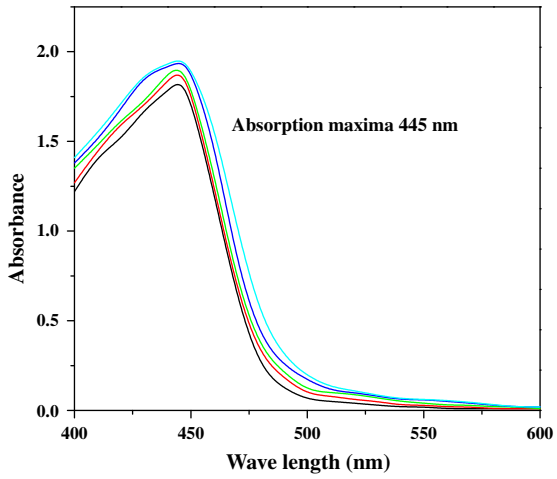


Fig. 4. Absorption spectra of picric acid (1×10^{-2} M) in methanol with addition of 1-Naphthylamine concentrations ranging from 0.1 M to 0.3 M are shown with increasing concentrations bottom to top.

maxima ($\lambda_{CT} = x_c$) and the corresponding transition energies (hv) are summarized in Table 2.

3.2. Determination of ionization potentials of the donor

The ionization potentials of the donor (I_D) in the charge transfer complex are calculated by using empirical equation derived by Aloisi and Pignataro [22]

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

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

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 by using the formula

$$f = 4.32 \times 10^{-9} \int \varepsilon_{CT}\, dv \quad (2)$$

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

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

where ε_{CT} is the maximum extinction coefficient of the band and $\Delta v_{1/2}$ is the half-width, i.e., the width of the band at half of 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

$$\mu_{EN} = 0.0952\ [\varepsilon_{CT} \Delta v_{1/2} / \Delta v]^{1/2} \quad (4)$$

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

3.4. Determination of resonance energy (R_N)

Briegleb and Czekalla [23] theoretically derived the relation to obtain the resonance energy given as below:

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

where ε_{CT} is the molar extinction coefficient of the complex at the maximum of the CT absorption, v_{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 complex under study are given in Table 2.

3.5. Determination of standard free energy changes (ΔG^o) and 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 using the equation derived by Martin et al. [24]

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

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

The energy (E_{CT}) of π–π^* interaction between donor (NPA), and acceptor, (PiOH), is calculated by using the equation derived by Briegleb [25]

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

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

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

3.6. Spectrophotometric study of formation constants of the charge transfer complex 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 [26,27]. The spectrophotometric data was 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 [26,27] equation in the form.

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

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, Eq. (8) [26,27] is valid under the condition $[D]_o \gg [A]_o$ [19,20] for 1:1 donor–acceptor complex. The concentration of the donor (NPA) was changed over a wide range from 0.1 M to 0.3 M while concentration of π-acceptor PiOH was kept fixed at 0.01 M in each reaction mixture. These produced solutions with donor:acceptor molar ratio vary from 10:1 to 30:1.

The Benesi–Hildebrand [26,27] 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 complex of NPA with PiOH in different polar solvents at room temperature is reported in Tables 1 and 3. In all the systems, good linear plots according to Eq. (7) [26,27] are obtained, shown in Fig. 5. Formation constants for the complex in different polar solvents at room temperature determined from the Benesi–Hildebrand plots are summarized in Table 3. The correlation coefficients of all such plots were more than 0.95. Plots of $[A]_o/A$

Table 1
Gaussion curve analysis for the CTC in spectrum 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
CTC absorption maxima (λ_{CT}), transition energies ($h\nu_{CT}$) of PiOH complex, experimentally determined ionization potential (I_D) of the donor, oscillator strength (f), transition dipole strengths (μ_{EN}) and resonance energy (R_N) of complex.

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

Table 3
Data for spectrophotometric determination of stoichiometry, absorption maxima (λ_{CT}) and association constant (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	$[A]_o$ M	Absorbance at λ_{CT} (nm)	λ_{CT} (nm)	K_{CT} (l mol^{-1})	ε_{CT} (1 mol^{-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	0.01	1.843			
			0.15		1.894	445	107	202
			0.2		1.915			
			0.25		1.945			
			0.3		1.960			

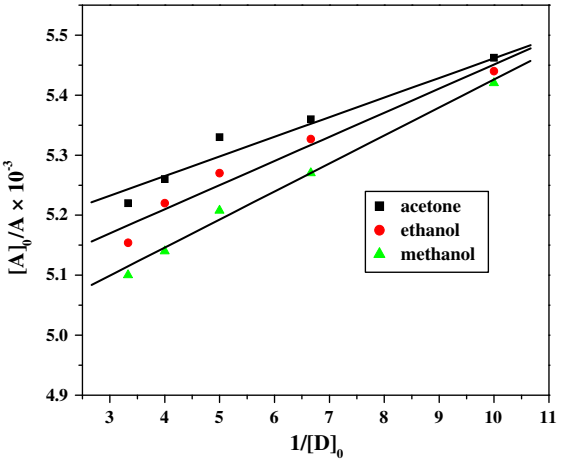


Fig. 5. Relation between $[A]_o/A$ and $1/[D]_o$ of PiOH + NPA in acetone, ethanol, methanol.

against $1/[D]_o$ were found to be linear in all the systems are shown in Fig. 5 for 1:1 charge transfer complex, i.e., the straight lines are obtained with the slopes $1/K_{CT}\varepsilon_{CT}$. These results suggest the formation of the 1:1 CT complex. From slope $1/K_{CT}\varepsilon_{CT}$ and intercept, $1/\varepsilon_{CT}$, K_{CT} and ε_{CT} of the complex were calculated.

3.7. Effect of solvents on the formation of CT complex

The experimental results of the CT interaction between PiOH with NPA in different polar solvents show the values of association constants as K_{CT} 157(l mol^{-1}) in acetone, 117(1 mol^{-1}) in ethanol, and 107(1 mol^{-1}) in methanol and the values of molar extinction coefficient ε_{CT} 194(1 mol^{-1}cm^{-1}) in acetone, 198(1 mol^{-1}cm^{-1}) in ethanol, and 202(1 mol^{-1}cm^{-1}) in methanol. The spectroscopic properties were markedly affected by the variation in solvent polarity. 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, CT complex is stabilized in less polar solvent [28]. Dissociation of the complex into $D^+ - A^-$ radicals have been found to occur in the ground state [29]. 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) is 2.22×10^{-5} in acetone, 2.77×10^{-5} in ethanol, and 2.45×10^{-5} in methanol, the values of transition dipole moment (μ_{EN}) is 0.936 (Debyes) in acetone, 0.946 (Debyes) in ethanol, and 0.955 (Debyes) in methanol, and values of resonance energy R_N (eV) is 0.0072 in acetone, 0.0072 in ethanol, and 0.0074 methanol, (given

in Table 2) indicate that the complex should be stable in less polar solvent (acetone). The very low values of f indicate the neutral character of CT complex in their ground state.

The parameters thus obtained are presented in Table 4. These values show that the complexation is thermodynamically favored. The free energy change of the complexation also reveals that the CT complex formation between donor (NPA) and acceptor (PiOH) is of exothermic nature. The values of ΔG^o for complexation in acetone, ethanol, and methanol are given in Table 4. The values of ΔG^o tend to be more negative as the association constants for CT complex increases. This is because of the fact that as the bond between the components becomes stronger so that the components are subjected to more physical strain or loss of freedom, resulting is the more negative values of ΔG^o.

The ionization potentials I_D (eV) of the donor can be calculated by using the experimentally determined λ_{CT} of the CT complex from Eq. (1) [22]. The calculated values of I_D in acetone, ethanol, methanol are shown in Table 5. The approximate constancy of I_D values, indicate that the ionization potential show a negligibly small effect on K_{CT} values.

3.8. Comparative study of FTIR spectra of CT complex and reactants

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.

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

Systems	Solvents	K_{CT} (l mol^{-1})	$-\Delta G^o$ (298 K) (kJ mol^{-1})	r
PiOH + NPA	Acetone	157	12.495	0.971
PiOH + NPA	Ethanol	117	11.754	0.947
PiOH + NPA	Methanol	107	11.525	0.991

Table 5
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

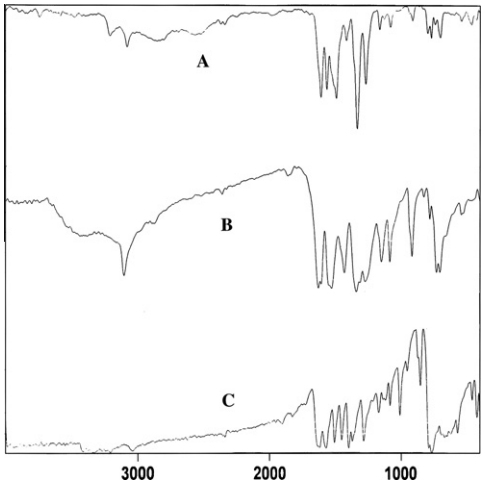


Fig. 6. FTIR spectrum of (A) complex of NPA and PA, (B) acceptor PA and (C) donor NPA.

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

PiOH	NPA	Complex	Assignments
3104s, br	3409br	3209br	ν(O—H), PA
–	3338br	3083br	ν(N—H), NPA ν_{as} (C—H), CH_3 + CH_3 ν(C—H), aromatic ν ($^+$NH)
–	3206br		
2870w	3043br	–	
–		2845br 2591br	Hydrogen bonding b/w —OH—H—NH
1633vs	–		
1606ms	1623vs	1608ms	$\nu_{as}(NO_2)$, PA
1531br	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), $\nu_s NO_2$, PA
1343vs	–	–	ν_{as}(C—N)
1277vs	1287vs	1267br	ν(C—O)
1150ms	1170w	1165ms	
1089ms	1083br 1012sharp	1083ms	ν_s(C—N)
916ms	951sharp	936sharp	δ(C—H) in plane bending
830w 783sharp	854sharp	915sharp	δrock, +NH_2 CH_2 rock skeletal vibrations
	763vs	768vs	C—H out of plane bending
727ms	666vs	697ms	
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.

The FTIR spectrum of picric acid shows a peak at 3104 cm^{-1} due to ν_{OH} vibrations whereas the FTIR spectrum of 1-Naphthylamine show a number of peaks at 3409–3043 cm^{-1} due to ν_{NH2} vibrations. As a result of complexation vibrational frequencies of OH, NH_2 bands are broadened and shifted to lower wave number (3209–2591 cm^{-1}) [30]. In the FTIR spectrum of complex the broadened peaks occurred at 2845 cm^{-1} and 2591 cm^{-1} region are due to hydrogen bonding in the complex. These 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 is stabilized by hydrogen bonding.

3.9. ^{1}H NMR spectrum of CT complex

The ^{1}H NMR spectrum of CT complex 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. The signal is split into triplet by two neighborhood proton one 8.571 ppm [31]. The triplet peaks at δ = 8.032 ppm is due to the C_1, C_2 and C_3 carbon atom of 1-Naphthyl amine and the doublet peak 7.793 ppm is assigned to the proton on C_4, C_5 carbon atom of 1-Naphthyl amine moiety in the complex. The same were observed 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 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 [31] which are absent in spectrum on CT complex. These shifts

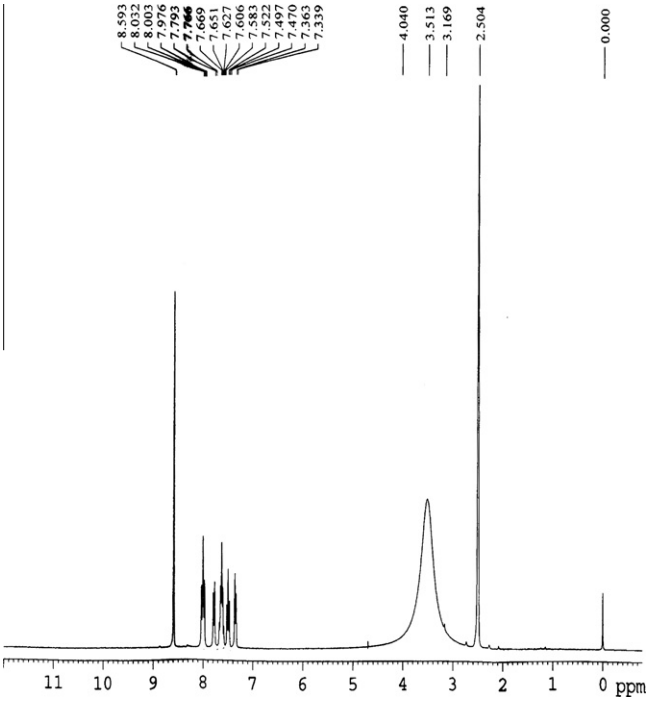
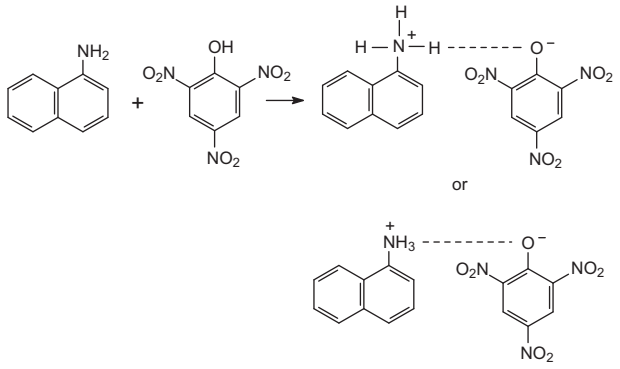


Fig. 7. ^{1}H NMR spectrum of complex.



Scheme 1. Mechanism for interaction between 1-Naphthylamine with picric acid.

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.

4. Conclusions

The UV–Vis spectrophotometric method for the study of CTC of picric acid with 1-Naphthylamine reveals the formation of 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 spectroscopic and thermodynamic parameters of the complex were found to be solvent 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 ^{1}H 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 —H atom of amino group of 1-Naphthylamine.

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