INFRARED, RAMAN, ELECTRONIC SPECTRAL STUDIES AND EFFECT OF pH OF 4–CHLORO–3–NITRO PHENOL AND 2–CHLORO–4–NITRO PHENOL

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Abstract: The present research paper confined in reporting the investigations of infrared, laser Raman and ultraviolet spectra of 4–chloro–3–nitro phenol and 2–chloro–4–nitro phenol in their respective region. The spectra have been analyzed according to the assumption of C_s point group symmetry and complete vibronic interpretation including assignment of fundamental and group modes [ground and excited state] with effect of substituents are determined. The effect of pH variation on electronic transitions of these compounds in ethanol solvent has been studied. The electronic transition viz. n–π*, n– π* and n–□□□have also been discussed along with red and blue shift.

Keywords: IR, Raman spectra, Electronic spectra, pH effect

INTRODUCTION

 Spectroscopic studies such as infrared, Raman and ultraviolet are widely used in biophysics research on nucleic acid and related compounds. The electronic spectra of phenol and some of its mono and disubstituted phenols have been studied extensively in recent years [4-6]. The electronic transition in phenol exhibit two band system in the near UV region, one towards the longer wavelength side desinated as n– π* transition and other towards the shorter wavelength side designated as n– π* transition. The electronic spectra of substituted nitro and hydroxy group also appear in literature [8,9]. In view of these, the present research paper the infrared, laser Raman and ultraviolet spectrum with their complete assignments, ground and excited state fundamentals corresponding to all modes of vibration of 4–chloro–3–nitro phenol and 2–chloro–4–nitro

phenol. Its appear that no preview reports has been found on infrared, laser Raman and ultraviolet spectrum of both the molecules cited above.

Experimental and Computational details

98% spec–pure compounds 4–chloro–3–nitro phenol and 2–chloro–4–nitro phenol (here after reffered as 4,3–CNP & 2,4–CNP) were obtained from M/s Sigma Aldrich Chemie, West Germany and used as such without further purification. However their purity was confirmed by elemental analysis and melting point determination [126–128° & 105–108°]. The infrared absorption spectra were recorded on Perkin–Elmer spectrophotometer model–52 in the region 400–4000 cm^{-1} in nujolmull. While, the laser Raman spectra of the title compounds were recorded on "Spex Rama Lab" Spectrophotometer using 52 mg argon krypton laser beam of wave length 488 nm in the region 50–4000 cm^{-1}.

The experimental technique in the ultraviolet spectra of both compounds were recorded on Beckman spectrophotometer model–35 in the region 200–350 nm. The spectra have been recorded in various solvents (viz. ethanol, methanol and water). The concentration of the solution in all the cases was kept constant (8×10^{-3} gm/litre). All the solvents used was of spectroscopic grade. The ratio of pure solvent was obtained at 9 : 1 by volume.

RESULTS AND DISCUSSION

The molecular structure of 4,3–CNP and 2,4–CNP are shown in figure-1. The infrared and laser Raman spectra of 4,3–CNP and 2,4–CNP are shown in figure 1.1, 1.2 and figure 1.3, 1.4 respectively. Furthermore the observed vibrational frequencies of both the compounds along with their relative intensities and probable assignments are presented in Table–1.
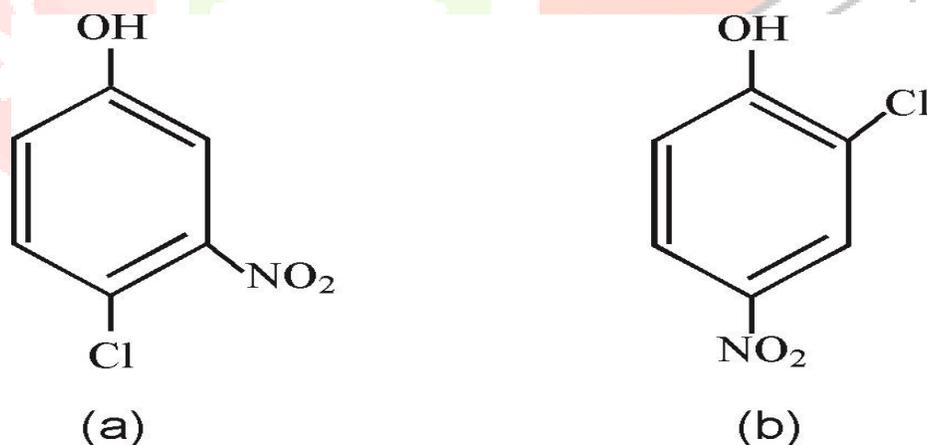

Fig.–1 Molecular structure of (a) 4, 3–CNP and (b) 2, 4–CNP.

The observed spectra are explained on the basis of C$_S$ point group of the molecules. On the other hand, the ultra violet absorption spectra of 4,3–CNP and 2,4–CNP is different solvents (viz. ethanol, methanol and water) are shown in fig. 1.5 and in fig. 1.6 respectively. The complete analysis of ultraviolet absorption spectra of both the molecules is presented in Table–2. In addition to the above, the assignments of the spectra have been made in analogy with substituted phenol and substituted benzene derivatives proposed by various workers [10, 11]. The infrared, laser Raman and ultraviolet spectral analysis not only give the frequencies of the bond observed but also give the knowledge of the intensity of various bonds. The absolute of a vibrational (IR &

Raman) band is related to the change of electronic moment during the vibration and in the case of small molecules it is sometimes possible to derive from the determined absolute intensity, the individual bond moment and thus gain some intimate knowledge of molecular electronic structure [12, 13].

VIBRATIONAL SPECTRA

RING VIBRATIONS:

C–C Vibrations: In all substituted benzene, a group of three bands is usually observed in the region 1400–1650 cm^{-1} [11, 14, 15]. In general the bands are variable intensity and are observed at 1625–1590 cm^{-1}, 1590–1570 cm^{-1}, 1540–1470 cm^{-1} and 1465–1648 cm^{-1} from the frequency range given by Rao [10], for the three bands in the region. In the present investigation, the infrared bands observed at 1439, 1484, 1584, 1636 cm^{-1} and 1433, 1483, 1600, 1620, 1648 cm^{-1} in 4,3–CNP and 2,4–CNP respectively have been taken to represent C–C stretching modes. While C–C in–plane bending modes appear in the region 1300–1400 cm^{-1} in the case of trisubstituted benzene [9, 16]. In the present study the infrared bands observed at 1337, 1357 cm^{-1} with Raman bands at 1332, and 1352 cm^{-1} and 1333, 1363 cm^{-1} in both the compounds have been assigned to the above modes. The C–C out–of–plane bending which are umbralla vibrations are observed in the region 700–800 cm^{-1}. The infrared bands observed at 766 cm^{-1} in both the molecules with Raman band at 764 and 763 cm^{-1} have been taken to represent C–C out–of–plane bending mode. Also the Raman bands observed at 1026 and 1020 cm^{-1} in both the compounds have been assigned to trigonal bending modes. Inspite of them, the out–of–plane bending of C–C–C is also possible for infrared and Raman spectra have been assigned in Table–1 [17, 18, 19].

C–H Vibrations: The molecules 4,3–CNP and 2,4–CNP are trisubstituted benzene and only three hydrogen atoms are left in the ring. These may be rise to three C–H stretching vibrations. While the other three frequencies in both the molecules depends on the mass and nature of the substituent's. The C–H stretching vibrations will be essentially similar to that of benzene. According to Bellamy [9] and other [20,21] the multiple absorption band in the vibrational (IR & Raman) spectra of phenol in the region 3000–3100 cm^{-1} are due to C–H stretching vibrations. Herzberg [8] have suggested that C–H in–plane bending in the region 1000–1300 cm^{-1} and C–H out–of–plane bending vibration in the region 750–1000 cm^{-1}. In the present investigation, the infrared bands observed at 3030, 3094 cm^{-1} and 3060 cm^{-1} with Raman band at 3020 cm^{-1} and 3052, 3092 cm^{-1} in 4,3–CNP and 2,4–CNP respectively have been taken to represent C–H stretching modes. In view of these assignments, the infrared bands observed at 1128, 1118 cm^{-1} with the counterpart of Raman values obtained at 1133, 1120, 1139 cm^{-1} respectively have been assigned to C–H in–plane bending modes and similarly the infrared band at 900, 890 cm^{-1} with Raman band at 901 cm^{-1} have been assigned to C–H out–of–plane bending vibrations (Table–1). These assignments are in good agreement with the literature values [22-24].

C–X Vibrations (X = –OH, –NO$_2$, –Cl)

C–OH Vibrations: Tripathi [25] have suggested the occurrence of X–sensitive vibration near at 1300 cm^{-1} in the substituted benzene [26–28]. In the present study, the C–OH stretching vibrations occurs at 1300 cm^{-1} in infrared with Raman band at 1292 cm^{-1} and 1310 cm^{-1} in both the compounds. The C–OH in-plane bending

infrared vibration has been observed at 584 cm^{-1} and Raman band at 588 cm^{-1} in 4, 3–CNP and Raman band at 578 cm^{-1} in 2, 4–CNP. This find support from the work of Singh [29]. The frequency around 380 cm^{-1} and 382 cm^{-1} in Raman band have been assigned to C–OH out–of–plane bending vibration by many investigators [30–33].

C–NO$_2$ Vibrations: The C–NO$_2$ stretching vibration appears near 1100 cm^{-1} in the spectrum of nitro benzene [10, 26, 34]. In the present investigation, the infrared bands observed at 1050 cm^{-1} and 1051 cm^{-1} with Raman band at 1053 cm^{-1} have been assigned to the above mode [35]. The C–NO$_2$ in–plane bending vibration are observed at 324 cm^{-1} and 319 cm^{-1} in Raman band and C–NO$_2$ out–of–plane bending vibration appear at 120 cm^{-1} in 4,3–CNP and 2,4–CNP respectively [36–39].

C–Cl Vibrations: C–Cl stretching mode have generally been assigned in between the range 550–750 cm^{-1} in substituted benzene [40,41]. Since the compounds are monochloro substituted, the one C–Cl frequency is expected in the molecules. In the present case, the infrared bands observed at 686 cm^{-1} and 670 cm^{-1} with Raman band at 684 cm^{-1} and 667 cm^{-1} in 4,3–CNP and 2,4–CNP have been assigned the above modes. The C–Cl in-plane bending only Raman band observed at 337 cm^{-1} and 340 cm^{-1} in both the molecules. Vipin [39] have suggested the frequencies between 150–250 cm^{-1} to C–Cl out-of-plane bending vibrations in various chloro substituted benzene. The Raman frequency of 210 cm^{-1} and 215 cm^{-1} have been assigned to the above mode. The present in–plane and out–of–plane bending C–Cl bending modes are supported by literature values [42–45].

Group Vibrations

–OH Vibrations: Bellamy [9], Rao [10] and Suzuki [44] suggested the OH valence oscillations in the region 3500–3700 cm^{-1} for the molecule containing OH group. Kalsi [45] and Varsanyi [11] pointed out these vibrations about 3600 cm^{-1}. The OH group has one stretching, one in–plane bending and one out–of–plane bending. In the present investigation the Raman bands observed at 3538 cm^{-1} and 3530 cm^{-1} in 4,3–CNP and 2,4–CNP respectively have been assigned to the above modes.

The frequency due to in–plane bending vibrations in phenol, in general lies in the region 1150–1250 cm^{-1} [46–49]. This vibration was found in a narrow region. In the present case, the infrared band observed at 1235 cm^{-1} and 1233 cm^{-1} with Raman band at 1227 cm^{-1} have been assigned to represent OH in–plane bending vibration in the compounds. The OH out–of–plane bending infrared band observed at 720 cm^{-1} and Raman band at 705 cm^{-1} and 729 cm^{-1} in 4,3–CNP & 2,4–CNP respectively. The frequency increase with hydrogen bond strength because of the larger amount of energy required to torsion OH band in Raman at 406 cm^{-1} [36, 47, 50].

–NO$_2$ Vibration: Yadav [46] have suggested the NO$_2$ group absorb strongly at 1600–1650 cm^{-1} called asymmetric nitro group and some what more 1400–1500 cm^{-1} called symmetric nitro group [51–53]. The usual o–m–p bands at 700–900 cm^{-1} are upset in nitro aromatic and not very reliable, probable due to interaction with the out–of–plane NO$_2$ bending frequency. In the present study, the infrared bands observed at 1584 cm^{-1} and 1600, 1620 cm^{-1} and in Raman bands at 1590, 1616 cm^{-1} and 1595 cm^{-1} have been assigned to the

asymmetric nitro group in both the compounds respectively. While only infrared band observed at 1484 cm^{-1} and 1483 cm^{-1} in 4,3–CNP and 2,4–CNP have been assigned to the symmetric nitro group [35, 37, 54].

Steric effect which destroy the nitro ring coplanerity thus reduce conjugation make aromatic nitro group resemble aliphatic nitro group. The nitro group compounds the bands at 835–890 cm^{-1}, 500–580 cm^{-1} and 110–120 cm^{-1} are defined as deformation, rocking and torsion modes respectively [14,44]. In the present study, the infrared band at 828 cm^{-1} and Raman bands at 828 cm^{-1} and 825 cm^{-1} in both the compounds is defined as NO$_2$ deformation mode. The infrared band at 538 cm^{-1} and 520 cm^{-1} with the Raman band at 538 cm^{-1} and 518 cm^{-1} have been assigned to NO$_2$ rocking mode. However, only Raman band at 120 cm^{-1} has been assigned to NO$_2$ torsion in 4,3–CNP molecule [10, 11, 55].

ULTRA VIOLET ABSORPTION SPECTRA

Rao[10] has suggested that changing of the solvent, effect the position of band in the electronic spectra, which may be used to identify the band as n–π*, π–π* and n–σ*. The n–π* transition of substituted benzene occur at distinct bands in the region 340–300 nm. Yadav[38] suggested that n–π* transition corresponds to out-of- plane transitions while π–π* and n–σ* in-plane transitions.

In view of this, for the molecules of 4,3–CNP and 2,4–CNP belonging at the point group C$_S$, the transition A$_{1g}$ → B$_{2u}$ in benzene becomes A$_{1g}$ → A$_{1u}$. It can be seen from Table–2 that the spectra of the two compounds have more or less similar vibronic structure. The same order of separation between the position of 0,0 bands of 4,3–CNP and 2,4–CNP is also found by comparing the spectra of these compounds [56-59].

Due to present investigation, the n–σ* transition at 210 nm (methanol) and π–π* transition at 228 nm in 2,4–CNP have been taken to represent in-plane transition, while the π–π* transition at 218 nm (ethanol and water), 224 nm (methanol) in 4,3–CNP have been represent in-plane transition. The n–π* transition bands around at 300 nm in trisubstituted benzene [11]. In view of these, the n–π* transition band around at 308 nm (ethanol, methanol & water) in 2,4–CNP have been taken to represent out-of-plane transition in the present investigation.

Solvent Effect

Generally, the solvent used in recording these spectrum are non-polar-one (like hexane) or polar solvents (like ethanol, methanol and water etc.). The band will be called blue shift or red shift [60-62]. According to the band shift towards shorter wavelength or longer wavelength on changing the solvent form hexane to water, then n–π* transitions are attributed to blue shift band while π–π* and n–σ* transition are attributed to red shift band. The amount of blue shift has been used as a measure of the strength of the H–bonding in ethanol, methanol and water and increase in transition energy. This energy required to weaken or break the hydrogen bond [63-65]. In the present investigation, the n–π* transition is blue shift in the compound 2,4–CNP with increasing polarity of the solvents (ethanol → methanol → water) as shown in Table–2 and in figure 2.6 and in figure 2.7 respectively. The red shift has been observed in the π–π* and n–σ* transitions in the said compounds with increasing polarity of the solvents are also given in Table–2. The attraction between

the solute and solvent molecule will be more if the polarity of the molecules will be more, which results the system more stable [36,41,44]. Thus, with increasing the dielectric constant of the solvent, the ionizing polarity of the solute molecule will be increase. Hence, grater the polarity of the solvents, greater will be the degree of the solution [66-68].

Effect of pH

Ultraviolet spectra sufficiently depict the electronic structure of molecule. In present study, there is a blue shift in the position of entire band with decrease in pH , the $n-\pi^*$ band is reported to shifted towards shorter wavelength in acidic solution by many coworkers [53,54].Recently Yadav [67] have suggested a blue shift in $n-\pi^*$ band with the addition of acid solution due to the binding of non-bonded electrons by protonation .In accordance with the above, we have observed a red shift in $n-\pi^*$ band with the addition of alkali in the aqueous solution of 4,3-CNP & 2,4-CNP shown in Fig.[2.8] and Fig. [2.9] and Table – 3.Yadav et al [69] have observed a red shift with the increase in pH in aniline. On increasing pH, a slight red shift $\pi-\pi^*$ band of the said compounds observed which is similar to the behavior observed in the literature [60, 6

TABLE-1.

ELEMENT OF INFRARED AND RAMAN SPECTRA OF 4-CHLOR-3-NITRO PHENOL AND 2–CHLORO–4–NITROPHENOL. (ALL VALUES ARE IN CM^{-1})

4-chloro–3–nitro phenol		2–chloro–4–nitro phenol		Assignments
IR	Raman	IR	Raman	
—	120 vw	—	—	NO_2 torsion
—	146 w	—	140 vw	γ (C–NO_2)
—	210 vw	—	215 ms	γ (C–Cl)
—	324 s	—	319 w	β (C–NO_2)
—	337 s	—	340 vw	β (C–Cl)
—	380 s	—	382 ms	γ (C–NO_2)
—	406 ms	—	—	(O–H) torsion
433 vw	432 vw	—	420 vw	β (NO_2)
—	450 w	465 vw	458 vw	γ (C–C–C)
538 vw	538 w	520 ms	518 w	NO_2 rocking
584 w	588 ms	—	578 vw	β (C–OH)
686 ms	684 vw	670 w	667 w	ν (C–Cl)
—	705 vw	720 ms	729 w	γ (O–H), γ (C–C)

766 w	764 vw	—	763 vw	γ (C–C)
828 s	828 w	—	835 w	γ (C–H), β (NO$_2$)
900 ms	901 w	890 ms	—	γ (C–H)
—	1026 vw	—	1020 vw	β (C–C–C) trigonal bending
1050 w	1053 ms	1051 ms	—	ν (C–NO$_2$)
—	—	1118 w	1120 w	β (C–H)
1128 ms	1133 s	—	1139 ms	β (C–H)
1300 s	1292 s	1300 s	1310 w	ν (C –OH)
—	1332 vw	1337 s	1333 s	β (C–C)
1357 s	1352 s	—	1363 s	β (C–C)
1439 ms	1444 ms	1433 ms	1427 vw	ν (C–C)
1484 ms	—	1483 s	—	ν (C–C), ν (NO$_2$) symm.
—	1544 ms	—	1548	ν (C–C)
1584 w	1590 s	1600 w	1595 s	ν (C–C), ν (NO$_2$) asymm.
—	1616 w	1620 vw	—	ν (C–C), ν (NO$_2$) asymm.
1636 vw	1628 ms	1648 vw	—	ν (C–C)
3030 w	3020 ms	3060 w	3053 vw	ν (C–H)
3094 ms	—	—	3092 w	ν (C–H)
—	3538 w	—	3530 vw	ν (O–H)

where,

ν = stretching   s   = strong

β = in-plane bending   ms   = medium strong

γ = out-of-plane bending   w   = weak

asym. = asymmetric   vw   = very weak

sym.   = symmetric def.   = deformation

TABLE–2.

SOLVENT EFFECT ON ULTRAVIOLET SPECTRA OF
4 - CHLORO-3-NITRO PHENOL AND 2-CHLORO – 4 - NITROPHENOL
(ALL VALUES ARE IN NM)

Solvent	DC*	RI**	4-chloro-3-nitro phenol				2-chloro-4-nitro phenol		
			$n-\pi^*$	$\pi-\pi^*$	$n-\sigma^*$		$n-\pi^*$	$\pi-\pi^*$	$n-\sigma^*$
Ethanol	25.0	1.3773	–	218	–		308	–	–
Methanol	32.0	1.3362	–	224	–		308	228	210
Water	80.5	1.3380	–	218	–		310	–	–

Where,   DC* = Dielectric Constant,

RI** = Refractive Index

TABLE–3.

EFFECT OF PH VARIATION ON ELECTRONIC TRANTION OF
4 - CHLORO-3-NITRO PHENOL AND 2-CHLORO-4-NITRO PHENOL
(ALL VALUES ARE IN NM)

Solvent	4-chloro-3-nitro phenol				2-chloro-4-nitro phenol		
	$n-\pi^*$	$\pi-\pi^*$	$n-\sigma^*$		$n-\pi^*$	$\pi-\pi^*$	$n-\sigma^*$
Ethanol	314	220	208		278	223	–
Ethanol+Hcl	287	221	–		268	213	–
Ethanol+ NaOH	302	230	–		268	217	–

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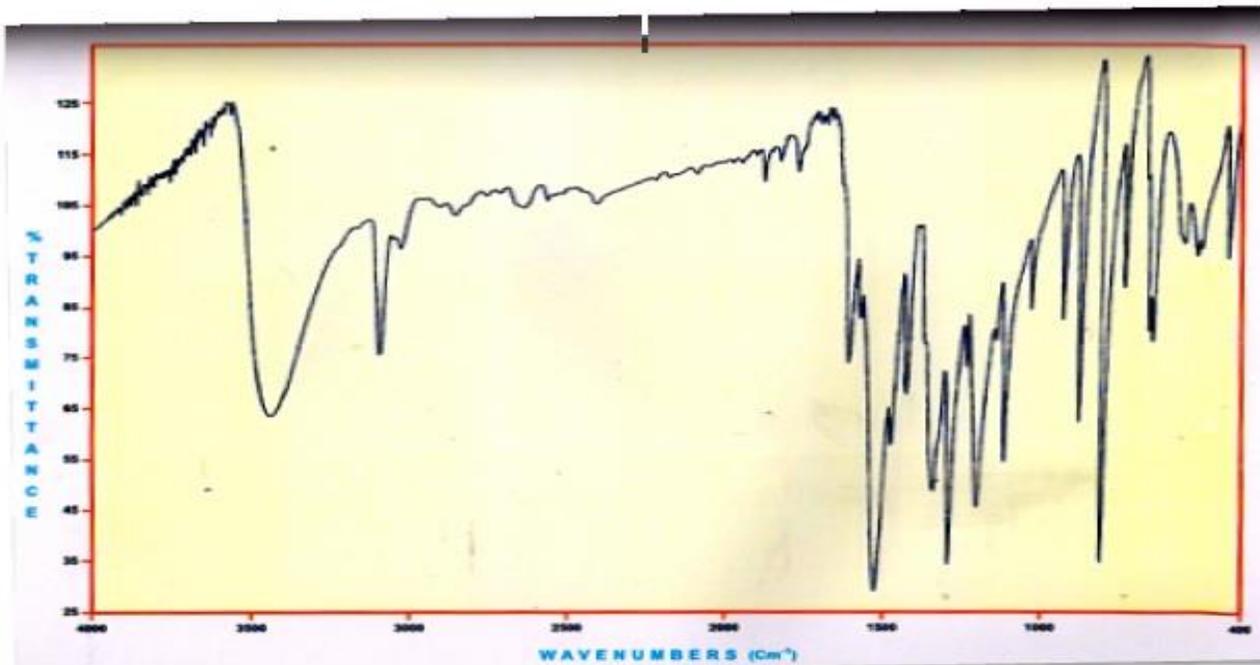
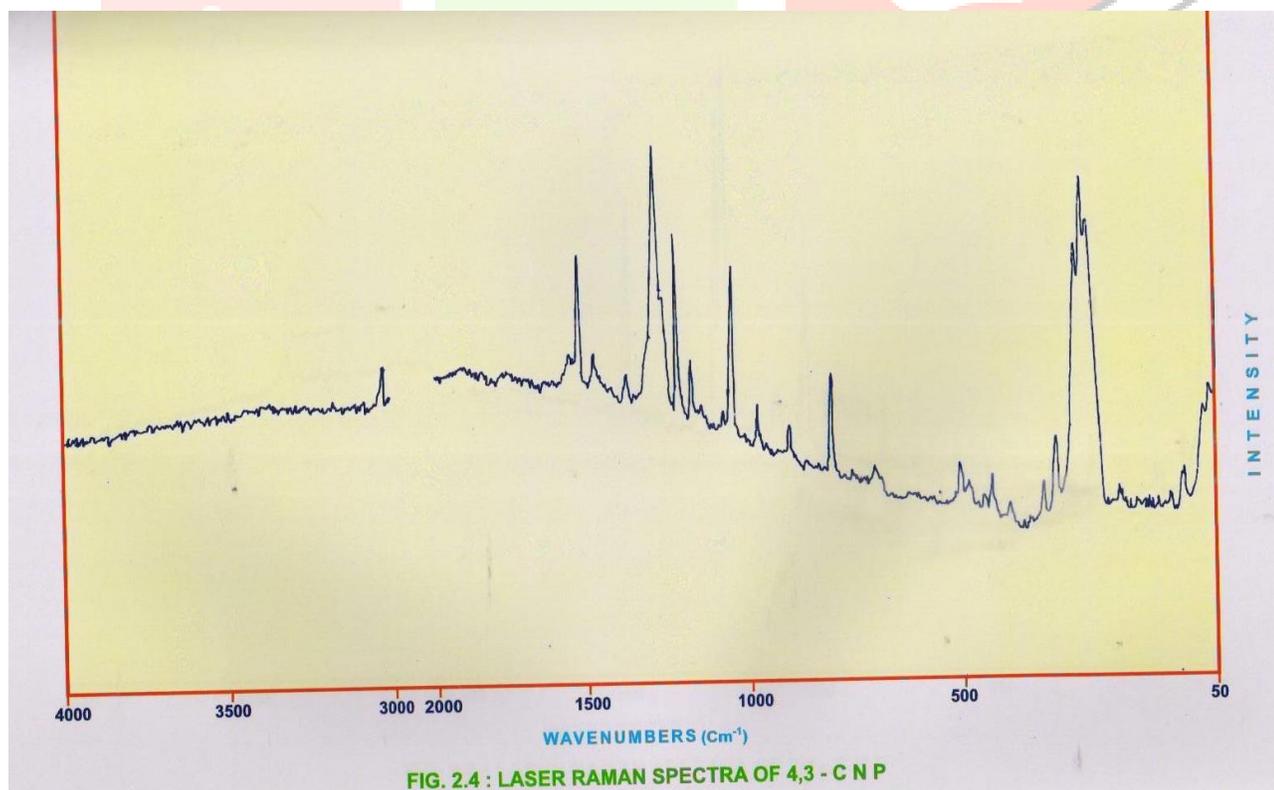Fig.1.1.Infrared spectra of 4,3-CNP IN Nujolmull

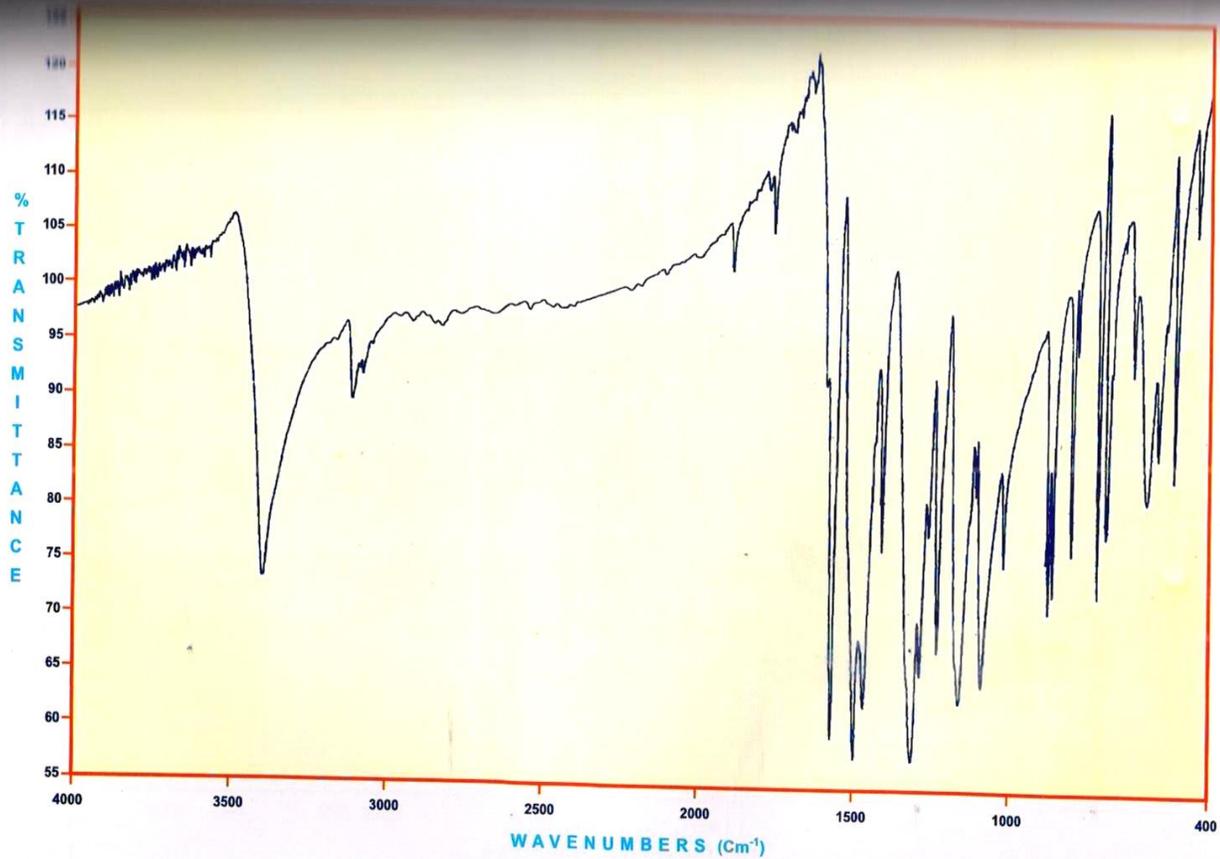FIG. 2.4 : LASER RAMAN SPECTRA OF 4,3 - C N P

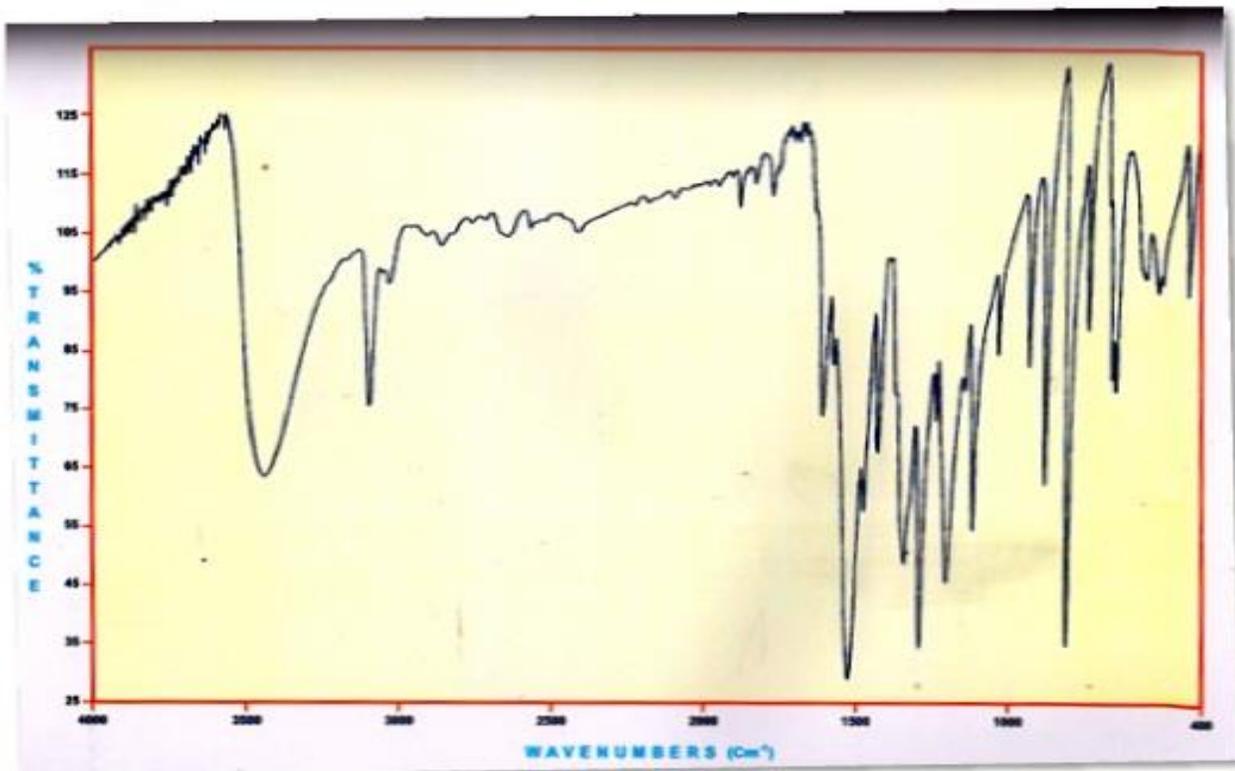FIG. 2.3 : INFRARED SPECTRA OF 2,4 - C N P IN NUJOLMULL
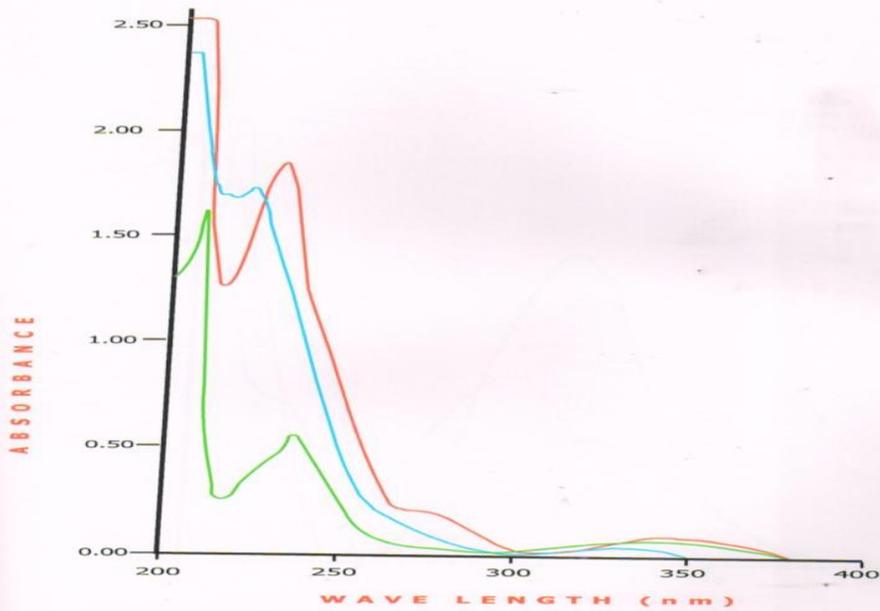

Fig.1.4: Laser Raman spectra of 2,4- CNP

Fig.2.6 : ULTRAVIOLET ABSORPTION SPECTRA OF 4,3–CNP IN
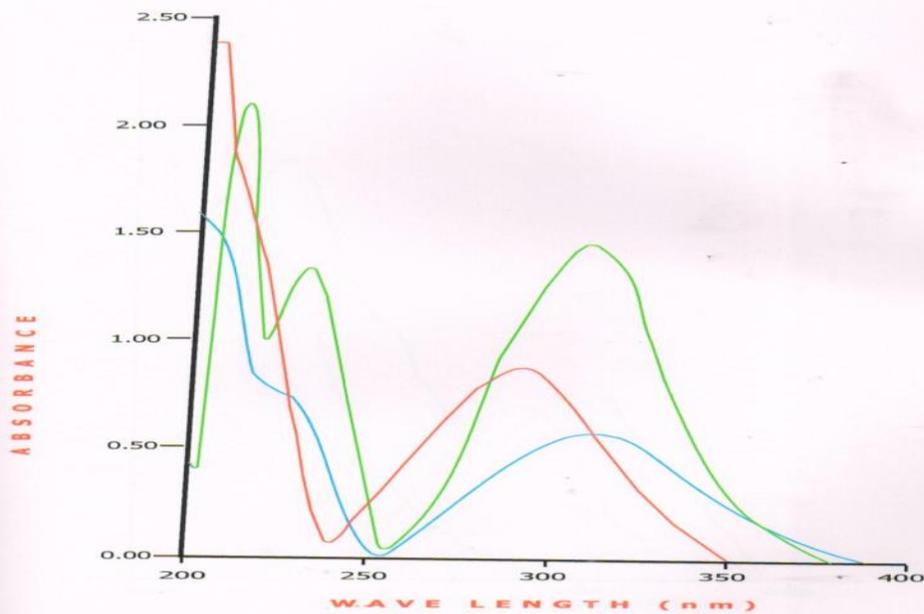(——) ETHANOL, (——) METHANOL AND (——) WATER

Fig.2.7 : ULTRAVIOLET ABSORPTION SPECTRA OF 2,4–CNP IN
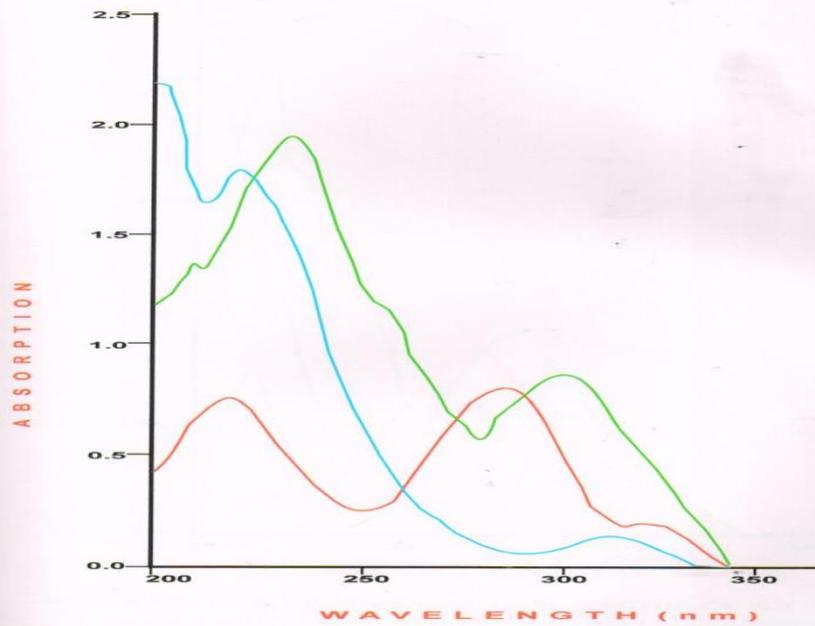(——) ETHANOL, (——) METHANOL AND (——) WATER

Fig.2.8 : ULTRAVIOLET ABSORPTION SPECTRA OF 4,3 -CNP IN ETHANOL: (———) NEUTRAL, (———) ACIDIC AND (———) ALKALINE MEDIUM
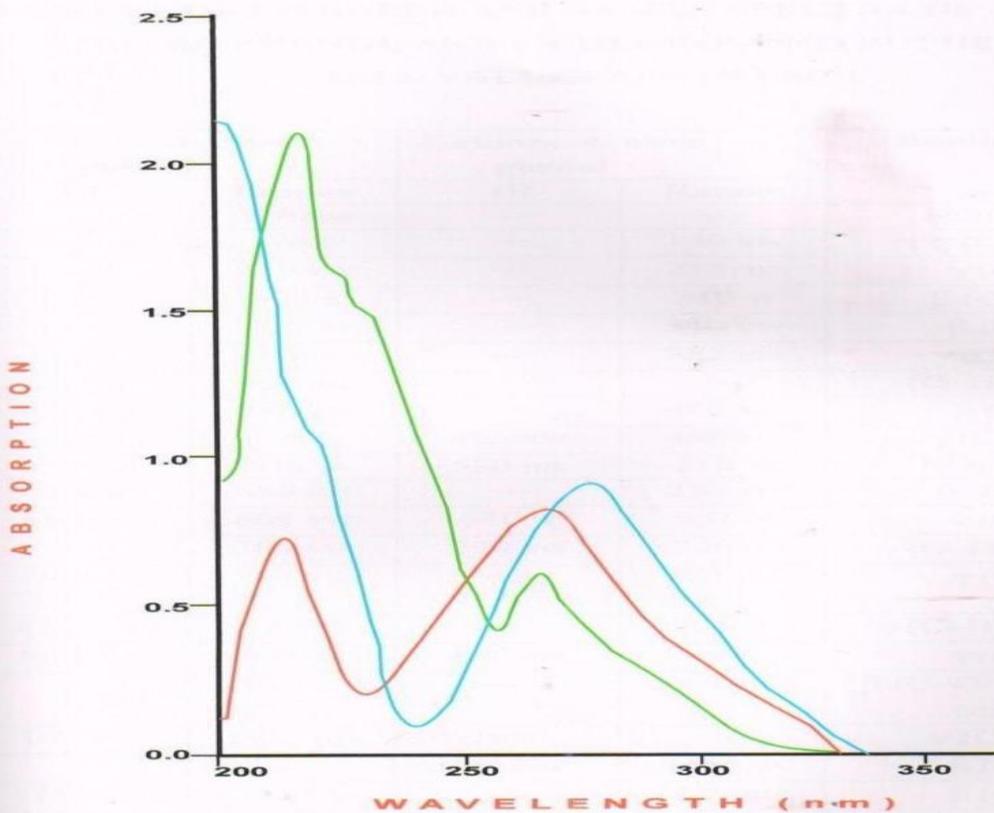

Fig.2.9 : ULTRAVIOLET ABSORPTION SPECTRA OF 2,4 -CNP IN ETHANOL: (———) NEUTRAL, (———) ACIDIC AND (———) ALKALINE MEDIUM