LASER RAMAN & FTIR SPECTRAL INVESTIGATION OF A BIOLOGICALLY ACTIVE SUBSTITUTED PYRIDINE MOLECULE

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ABSTRACT

An investigation on infrared absorption spectra (4000-400 cm^{-1}) and Raman effect (4000-50 cm^{-1}) of a biologically active molecule that is 4-amino-3,5-dichloro-2,6-difluropyridine are presented.The vibrational spectra are analyzed assuming C_{2v} point group for the molecule and in terms of fundamentals and their overtones.The assignments of the various bands are made on the basis of the magnitude and the relative intensities of the observed band.In the Raman and IR spectrum, the vibrations associated with NH$_2$ group show the hydrogen bonding and amine salt formation.The assignments made for the complex molecule under investigation are found to be satisfactory with the previous work on pyridine and benzene derivatives.

Keywords: Infrared spectra, Raman spectra, 4-amino-3,5-dichloro-2,6-difluoropyridine, KBr pellets, Nujolmull

I. INTRODUCTION

The N-heterocyclic molecules are reported as the immense medicinal and physiological importance. Thio-pyridine has been used in the treatment of tuberculosis[1], leproxy[2] and mental disordereness[3]. They are also known to act as herbicides, insecticides, rodenticides and plant growth regulator[4]. These have been reported to be the precursor for antidiabetic agent[5]. Although pyridine and their derivatives are of considerable biological importance, even then very little spectroscopic studies ate reported for them in literature. We have studied the vibrational and electronic spectra of 2-chloro-6-methoxypyridine[6]. In order to extend this work, the molecule 4-amino-3,5-dichloro-3,6-difluoropyridine has been undertaken at present for its vibrational studies, which is recently investigated a molecule of great biological importance[7]. In such type of molecule the role of substituent is very important. Owing to the low symmetry and also because of the limited information about the molecular parameters, reliable theoretical calculations for such molecules are not possible. Therefore, it was thought worthwhile to understand the role of the substituents by experimental methods. As the object of our investigation is to check the effect of substituents on the ring vibrations of 4-amino-3,5-dichloro-2,6-difluoropyridine molecule.

II. EXPERIMENTAL PROCEDURE

The spec-pure 4-amino-3,5-dichloro-2,6-difluoropyridine in sold phase was purchased from M/s Aldrich Chemicals, USA. Its infrared spectra were recorded on perkin Elmer M-500 FTIR spectrophotometer in the region 4000-400 cm^{-1} usingKBr and nujomull. Laser Raman spectrum in the region 4000-50 cm^{-1} was recorded on a Spex-spectrophotometer, using argon laser source with exciting radiations at 488ss nm.

III. RESULT AND DISCUSSION

The molecular structure of 4-amino-3,5-dichloro-2,6-difluoropyridine is shown in fig-1. Its Raman (4000-50 cm^{-1}) spectra is shown in fig-2. Whiletheinfrared absorption (4000-400 cm^{-1})spectra of the said molecule are shown in fig-3 and fig-4 using KBr pellets and nujolmull, respectively. The observed frequencies of 4-amino-3,5-dichloro-2,6-difluoropyridine along with their relative intensities and probable assignments are presented in table-1. The observed spectra are explained on the basis of C_{2v} point group for the molecule. The fundamental vibrations have been assigned to different modes on the basis of intensity consideration and expected magnitudes of the various observed frequencies. Much aid has been taken from the data available for similar molecules.

The vibrational assignments are discussed in the followingparagraphs :

3.1   Aryl ring vibrations

3.1.1   C-C vibrations

The C-C stretching frequencies in pyridine and its related compounds have been observed in the region 1630-1320 cm^{-1}. However an appreciable mixing of C-C and C-N stretching modes of vibrations take place due to the near equality of these vibrations. Under such circumstances the normal vibrations of the system cannot be identified with the vibration for a particular bond alone and thus the bands in this region are assigned to the nucleus as a whole. The IR bands observed 1605, 1490,1447/1617, 1540, 1522, 1507, 1456 cm^{-1} using KBr pellets/Nujolmull with the counterpart Raman bands observes at 1492, 1457,1410 cm^{-1} have been assigned to this modes. Inspite of that the strong IR band observed at 1396 cm^{-1} has been assigned to alternating ring stretch vibration of pyridine with the corresponding weak Raman band observed at 1395 cm^{-1}. All these modes find support by the literature values[8,9].

The in-planar carbon bonding vibrations are derived from nondegenerate b_{1u} (1010 cm^{-1}) and degenerate e_{2g} (606 cm^{-1}) modes of benzene. The non-degenerate b_{1u} (1010 cm^{-1}) has been observed at 1035/1014 cm^{-1} in IR spectra using KBr pellets/Nujolmull. The e_{2g} (606 cm^{-1})degenerate frequencies under C_{2v} symmetry have been observed at 651, 618, 600/650, 620, 600 cm^{-1} in IR spectra using KBr pellets/Nujolmull, while only twosuch vibrations occurred at 635, 608 cm^{-1} in Raman spectra of the 4-amino-3,5-dichloro-2,6-difluoropyridine[10].

The out of planar carbon bending vibrations are derived from the nondegenerateb_{2g} (703 cm^{-1}) and degenerate e_{2u} (404 cm^{-1}) modes of benzene. In the present work, the C-C out of plane bending vibrations have been observed at 736, 574, 430/722, 557,513 cm^{-1} in the IR spectra using KBr pellets/Nujolmull with the counterpart Raman frequencies observed at 548 and 422 cm^{-1}, which is in agreement with the literature[10].

3.1.2   Ring breathing mode and trigonal bending vibrations

The radial skeletal vibrations of benzene derivatives can, in principle, be divided into two groups: - the breathing or C-C-C bending vibrations and the C-X stretching vibrations. The separate division of these vibrations is however impossible due to the strong coupling of these modes[11]. Except the ring breathing

vibrations of benzene allthefrequencies are remaining practically unaffected by substitution. It has been pointed out by many workers that the reduced symmetry (C_{2v}), (C-C) breathing and (C-C-C) trigonal bending vibrations give rise to combined modified modes[12]. As a result one of the modified modes reduces to about 800 cm^{-1}, while the others keeps it self around 1000 cm^{-1} in substituted benzene[12]. In the present work, the broad IR bands observed at 1035, 966, 899/1014, 974, 942, 925, 896 cm^{-1} using KBr pellets/Nujolmull have been assigned to the coupled substituent stretching (C-X) and ring translational or ring breathing vibrations. Furthermore an IR band observed at 795 cm^{-1} using both KBr pellets and Nujolmull has been assigned to the coupled substituent bending and trigonal bending vibration. These modes are further verified by the literature[10-12].

3.1.3   Overtones of aryl ring vibrations

Usually intense overtones of aryl ring vibrations occur in the region 2000-1700 cm^{-1}. These bands are somewhat weaker than fundamentals and are most clearly seen in the spectra of moderately thick samples[13].in the present study', the IR bands observed in the region 2000-1700 cm^{-1} using KBr pellets/Nujolmull have been assigned to overtone of aryl ring vibrations.

3.2   C-X vibrations

In aryl halides there are no bands obviously comparable to the aliphatic C-X stretching bands due to interaction with ring vibrations. One ring vibrations that is X sensitive and involves some C-X stretching is found approximately at 1270-1100 cm^{-1} for aryl-F compounds[13]. The same band for aryl-Cl is found at1096-1089 cm^{-1} for para and 1078-1074 cm^{-1}for meta and 1057-1034 cm^{-1} for ortho substituted chlorobenzenes. In the present investigation, the bands observed at 1172, 1136/1178, 1139 cm^{-1} in IR spectra using KBr pellets/Nujolmull with the corresponding Raman band observed at 1183, 1148 cm^{-1} have been assigned to C-F stretching mode[11] and the only IR band found at 1075/1074 cm^{-1} to that of corresponding Raman band at 1062 cm^{-1} has been assigned to C-Cl stretching mode[9-14].

Fregason et al[15] assigned the C-F in-plane bending vibrations af p-tetrafluorobenzenes[11] to frequencies above 600 cm^{-1}. Moreover, according to these authors the vibrations of symmetry a_g (9a) has the frequency 832 cm^{-1}. Steel [16] assigns one of the C-F in-plane bending vibration to 641 cm^{-1i}in the spectrum of m-tetrafluorobenzene. When there several neighboring substituents vibrating in-phase the frequency will be very high[11]. In the present investigation, the IR bands observed at 795, 759/795, 756 cm^{-1} using KBr pellets/Nujolmull have been assigned to C-F in-plane bending mode. Out of these two IR bands only the second band is further supported by Raman band observed at 753 cm^{-1}. According to Varsanyi et al.[11], the in-phase vibrations of halobenzene, the frequency interval found is 400-150 cm^{-1}. Scherer et al.[17] assigned the C-Cl in-plane bending vibration to 320 cm^{-1} in pentachlorobenzene. In the present study the strong Raman bands observed at 336, 262 cm^{-1} have been assigned to this mode[10,12].

Steel et al.[18] in their study of the spectrum of pentafluorobenzene assigned only one of the out-of-plane C-F vibrations symmetry b_1 to 217cm^{-1}. This frequency is very close to the values for vibration 5 of sym-trifluorobenzene and 11 of hexafluorobenzene (214 and 215 cm^{-1}, respectively)[11]. In the present study, the strong Raman band observed at 215 cm^{-1} has been assigned to this mode. Furthermore the C-Cl out-of-plane bending mode is found in between 200-110 cm^{-1} in various chloro substituted benzene. In the present study, the Raman bands observed at 142, 114 cm^{-1} have been assigned to this mode[10,12].

Primary aromatic amines with the nitrogen directly on the ring absorbs strongly at 1330-1260 cm^{-1} due to stretching of the C_{aryl}-N bond[13]. According to Kalsi[8], aromatic amine generally shows two strong bands in between the region 1360-1180 cm^{-1}. The higher frequency is because the force constant of the C_{aryl}-N bond is increased due to resonance with the benzene ring. In the present investigation, the IR bands observed at 1382, 1320/1376, 1312 cm^{-1} using KBr pellets/Nujolmull have been assigned to this mode. Out of these two IR bands only the second band has been find support by the strong Raman band observed at 1330 cm^{-1}. This assignment is in agreement with those proposed for primary aromatic amines[19, 20]. Furthermore, the weak Raman band observed at 377 cm^{-1} has been assigned to C-NH_2 in-plane bending mode[21, 22] and the very strong Raman band observed at 231 cm^{-1} has been assigned to C-NH_2 out-of-plane bending mode[23].

3.3   Group vibrations

3.3.1   Amino group

According to Kalsi[8], the primary aromatic amines display two N-H stretching bands around 3500-3200 cm^{-1} (an asymmetric stretching band which is stronger of the two and a symmetric stretching band). In the present investigation, and IR band observed at 3331/3348 cm^{-1} using KBr pellets/nujolmull, which finds support by the weak but broad Raman band at 3340 cm^{-1} has been assigned to asymmetric N-H stretching mode and comparatively weak IR band observed at 3349/3380 cm^{-1} has been assigned to symmetric N-H stretching mode. The broadness and fine structure band (multiple peaks) further shows the presence of hydrogen bonding (we will discuss later on). These are in accordance with the empirical relation of Bellamy and Williams[24].

$$\nu_{sym} = 345.03 + 0.876 \, \nu_{asym}$$

this is found support by the literature[13, 25].

Furthermore silverstein et al[25] says that the N-H bending (scissoring) vibration of primary amines is observed in 1650-1580 cm^{-1} region of the IR spectrum. In this present study the IR band observed at 1624/1636 cm^{-1} Using KBr pellets/Nujolmull with the corresponding Raman band at 1622 cm^{-1} has been assigned to NH_2 scissoring deformation mode[8.9.25]. The NH_2 twisting frequency lies[21] around 10650 cm^{-1}. But in this present study, the interaction of similar frequencies (because of the presence of adjacent halogen groups) is possible that may modify these modes. Thus the IR band observed at 1114 cm^{-1} using Nujolmull has been assigned to this mode[23]. Which further find support by the Raman band observed at 1110 cm^{-1}. Still another N-H bending band display by primary and secondary amines are the N-H wagging at 900-600 cm^{-1} [8]. In this present investigation the IR band observed at 675 cm^{-1} with the corresponding Raman band at 664 cm^{-1}has been assigned to NH_2 wagging mode [21]. Furthermore, it was found that NH_2 torsion mode lie around 240-200 cm^{-1}. A strong Raman band observed at 215 cm^{-1} has thus been correlated to represent the NH_2 torsion mode[21,23] in the present case.

According to Kalsi[8], vibrational coupling occurs between two bonds vibration individually near same frequency and provided that the band are reasonably close in molecule. The coupling vibrations may both be fundamentals or a fundamental vibration may couple with the overtone of some other vibration. The later coupling is called Fremi resonance. In the present investigation, the IR band observed at 3213 cm^{-1} has been assigned to Fermi resonance band (with overtone of the band at 1622 cm^{-1} of N-H bending mode) using KBr pellets with counterpart Raman band at 3234 cm^{-1}, which find support by the literature value[8,13,25].

3.4   Amine salt vibrations

According to colthup et al[13], primary amine salts are characterized by strong absorption between 3200-2800 cm^{-1}due to asymmetric and symmetric NH_3^+ stretching. Aromatic amine salts absorbed at somewhat lower frequencies than aliphatic amine salts. In the present study, IR bands observed at 3139, 2926/3134, 2923 cm^{-1} using KBr pellets/Nujolmull have been assigned to this mode[8,25]. In addition between 2800-2000 cm^{-1}, there are a number of weaker combination bands, the most interesting of which is an isolated band usually near 2000 cm^{-1}, the intensity of which increases when the symmetry is reduced[13,25]. This band is assigned to a combination band the NH_3^+ torsion oscillation (about 1580 cm^{-1})[13]. In the present study, the IR band observed at 2216 cm^{-1} using KBr pellets has been assigned to this mode. Sharp band observed at 2236 cm^{-1} is also assigned to combination bands of NH_3^+ bending vibration[13]. According to Colthup et al.[13], the asymmetric $NH_3^{+\{}$ deformation absorbs at 15550-1505 cm$^{=1}$. In the present investigation, the IR bands observed at 1565/1576, 1558 cm^{-1} using KBr pellets/Nujolmull have been assigned to these modes. Which is further supported[25] by the Raman band observed at 1577 cm^{-1}.

3.5   Vibrations of hydrogen bonds

In 4-amino-3,5-dichloro-2,6-difluoropyridine compound the possibility of intermolecular H-bonding is greater than those intramolecular H-bonding because of high electronegative character of fluorine atom rather than chlorine atom also the five membered H-bonded ring (formed by intramolecular H-bonding, shown in fig-5(a)) is less stable than those six membered H-bonded ring (formed by intermolecular H-bonding, shown in fig-5(b)). Furthermore, according to colthup et al. [13], the presence of additional bands in the region 3700-3100 cm^{-1} are due to various N-H stretching vibrations and Kalsi[8] says, "when hydrogen bonding is operative the free N-H band is replaced by multiple bands". In this present study, the IR bands observed in the region 3700-3100 cm^{-1} have been assigned to N-H stretching mode that is further supported by the Raman band found in the similar region (Table-1)

Table 1 :- Assignments of vibrational frequencies of 4-amino-3,5-dichloro-2,6-difluoropyridine (All values are in cm⁻¹)

Raman		IR Frequencies				Assigments
Frequencies	(Intensity)	KBr	(Intensity)	Nujolmull	(Intensity)	
60	(s)					Lattice vibration
94	(vs)					Lattice vibration
114	(vw)					γ(C-CI)
142	(s)					γ(C-CI)
215	(s)					NH_2torsion,γ (C-F)
231	(vs)					γ(C-NH_2)
262	(s)					β(C-CI)
336	(s)					β(C-CI)
377	(w)					β(C-NH_2)
422	(vs)	430	(s)			γ(C-C),γ (C-N)

---				513	(vw)	Ring def. vibration
548	(vw)	574	(vw)	557	(vw)	γ(C-C)
608	(vs)	600	(s)	600	(w)	β(C-C)
		618	(w)	620	(vw)	β(C-C)
635	(w)	651	(s)	650	(w)	β(C-C)
664	(w)	675	(w)			NH_2 wagging
		736	(s)	722	(s)	γ ring
753	(vw)	759	(s)	756	(w)	β(C-F)
		795		795	(s)	β(C-F),(C-C-C) & (C-N-C) trigonal bending vibration
		899		896	(vwb)	ν(C-X) & ring translational (ring breathing) vibration
				925	(vw)	ν(C-X) & ring translational (ring breathing) vibration
				942	(vwb)	ν(C-X) & ring translational (ring breathing) vibration
		966	(vwb)	974	(vwb)	ν(C-X) & ring translational (ring breathing) vibration
		1035	(vwb)	1014	(vwb)	ν(C-X) & ring translational (ring breathing) vibration,β(C-C)
1062	(vw)	1075	(vs)	1074	(w)	ν(C-CI)
1110	(vw)			1114	(vw)	NH_2 twisting
1148	(s)	1136	(w)	1139	(vw)	ν(C-F)
1183	(vw)	1172	(vw)	1178	(vw)	ν(C-F)
1330	(s)	1320	(s)	1312	(wb)	ν(C-NH_2)
		1382	(vs)	1376	(vs)	ν(C-NH_2)
1395	(w)	1396	(s)			ν ring
1410	(w)					ν ring
1457	(vw)	1447	(vs)	1456	(vs)	ν(C-C),ν(C-N)
1492	(vw)	1490	(w)		(w)	ν(C-C),ν(C-N)
				1507	(w)	ν ring
				1522	(w)	ν ring
				1540	(w)	ν ring
				1558	(w)	Sym. NH_3^+ def. mode
1577	(vw)	1565	(s)	1576	(w)	Asym. NH_3^+ def. mode
		1605	(s)	1617	(s)	ν(C-C)
1622	(s)	1624	(vs)	1636	(w)	NH_2 scissoring

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		1690-1963	(vw)	1700-1965	(w &vw)	Overtones of aryl ring vibrations
		2216	(vw)			Combination band of NH_3^+ bending vibrations
		2636	(w)			Combination band of NH_3^+ bending vibrations
				2854	(s)	Band for Nuolmull
		2926	(vw)	2923	(vs)	νNH_3^+ (sym.) +Band for Nujolmull
		3139	(vw)	3134	(vwb)	νNH_3^+ (asym.)
3234	(vw)	3213	(w)			Fermi resonance band
3340	(wb)	3331	(s)	3348	(wb)	ν N-H (asym.)
3380	(vwb)	3349	(vws)	3380	(vws)	ν N-H (sym.)
				3434	(w)	ν N--H
3482	(vw)	3474	(s)	3488	(vw)	ν N--H
		3494	(w)			ν N--H

Where

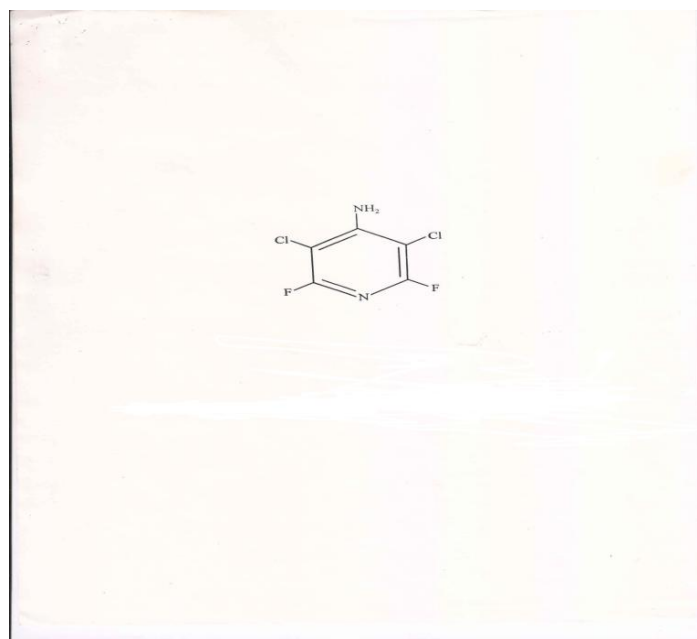|								
ν	=	Stretching	B	=	In-plane bending	γ	=	Out-of-plane bending
sym.	=	Symmetric	Asy.	=	Asymmetric	def.	=	Deformation
Vs	=	Very strong	S	=	Strong	Sb	=	Strong broad
W	=	Weak	Wb	=	Weak broad	Vw	=	Very weak
Vwb	=	Very weak board	Vws	=	Very weak shoulder			

Fig. 1 Molecular structure of 4-amino-3,5-dichloro-2,6-difluoropyridine
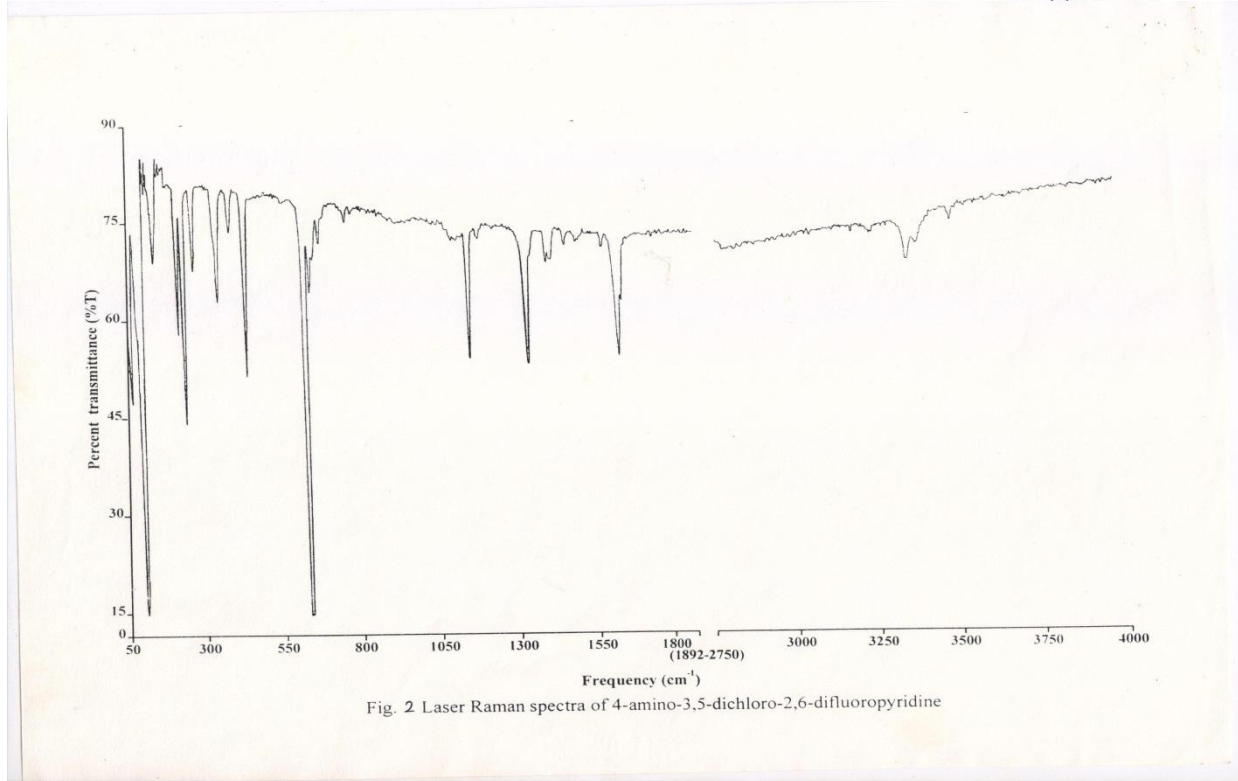
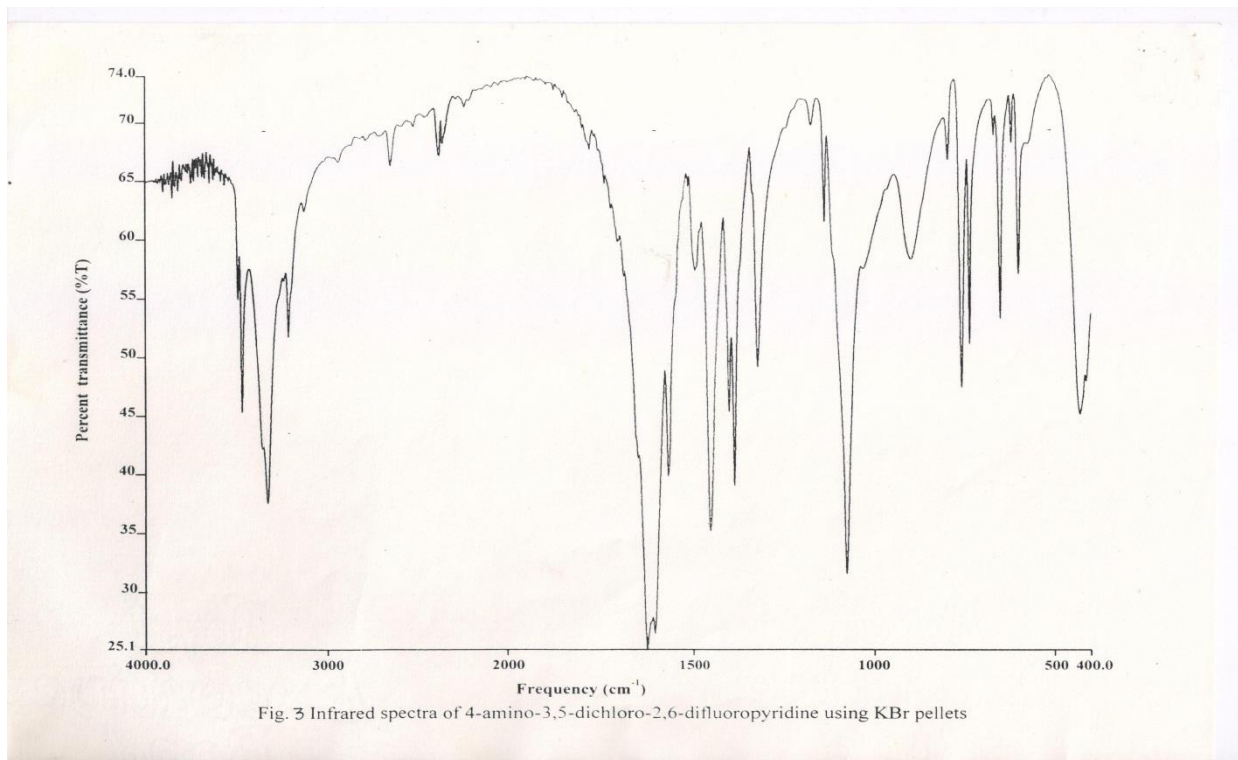Fig. 2 Laser Raman spectra of 4-amino-3,5-dichloro-2,6-difluoropyridine

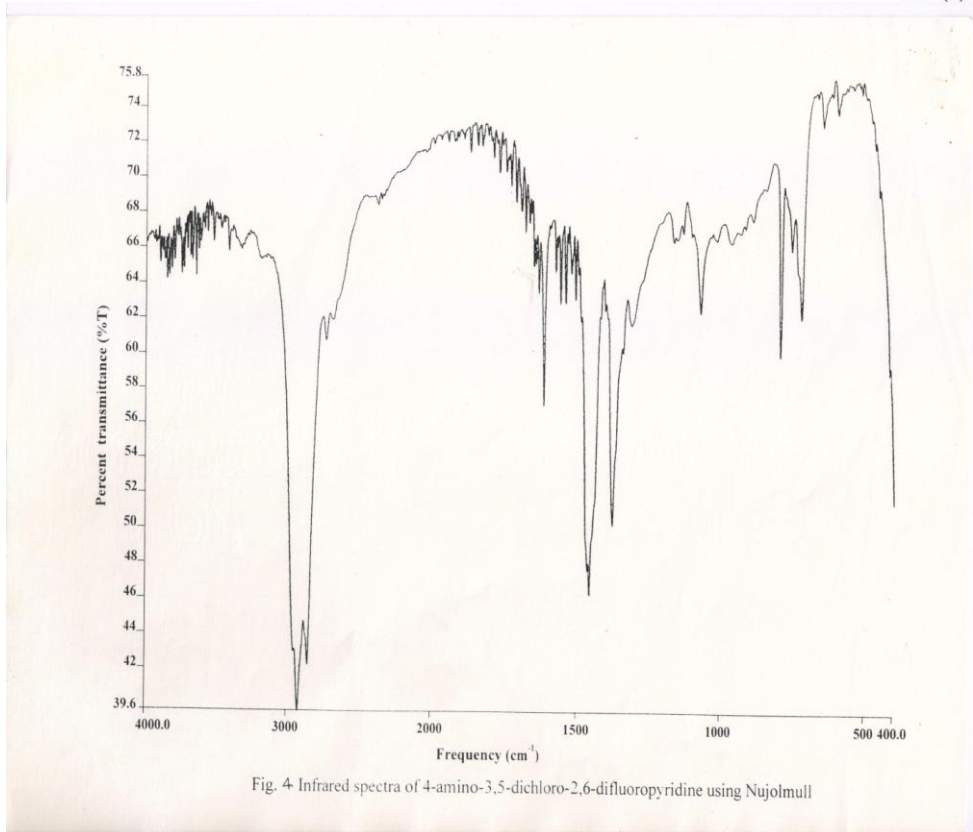Fig. 3 Infrared spectra of 4-amino-3,5-dichloro-2,6-difluoropyridine using KBr pellets

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Fig. 4 Infrared spectra of 4-amino-3,5-dichloro-2,6-difluoropyridine using Nujolmull

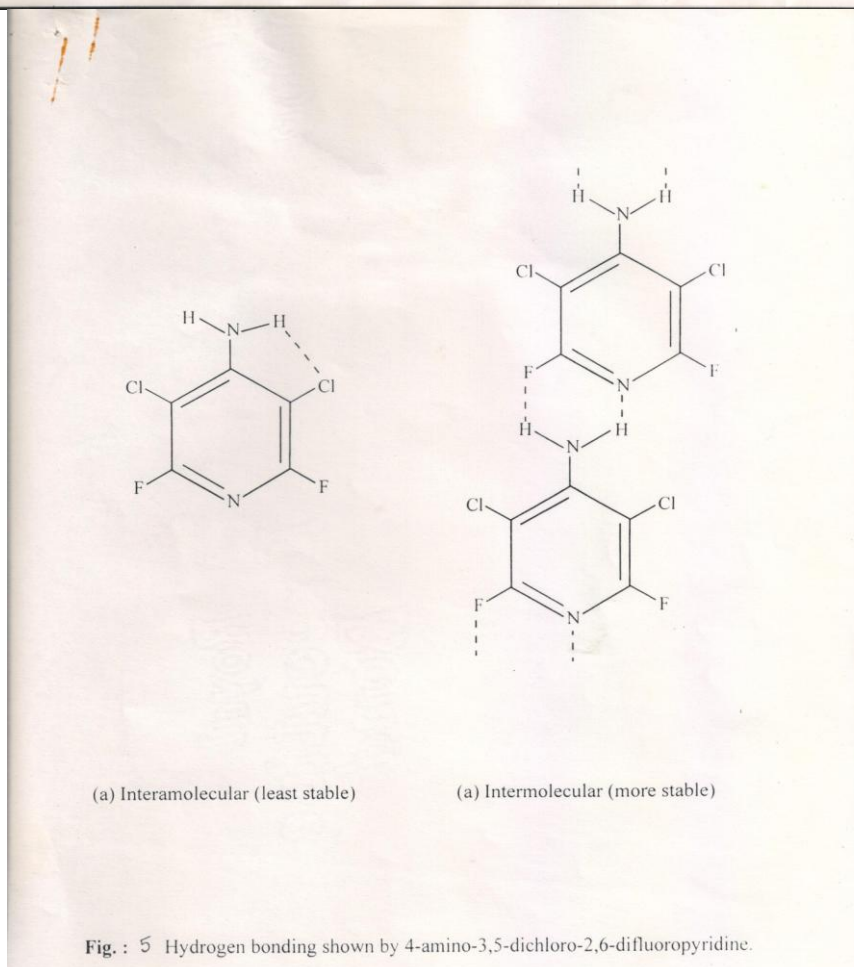(a) Interamolecular (least stable)   (a) Intermolecular (more stable)

Fig. : 5 Hydrogen bonding shown by 4-amino-3,5-dichloro-2,6-difluoropyridine.

IV.   CONCLUSION

The complete vibrational assignment and analysis of a biologically active molecule (4-amino-3,5-dichloro-2,6-difluoropyridine)[7] are investigated in this present study and the assignments made for the molecule are found to be satisfactory with the previous work on pyridine and benzene derivatives. This study is worthwhile to understand the role of substituents on various bond vibration by experimental method. Furthermore, in the Raman and IR spectrum, the vibration associated with NH_2 group show the hydrogen bonding and amine salt formation.

V. ACKNOWLEDGEMENT

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