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FT-IR and FT-Raman spectral analysis of 2-amino – 4,6-dimethylpyrimidine

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Abstract
Normal coordinate calculations of 2-amino-4,6-dimetylpyrimidine have been carried out using wilson's FG matix mechanism on the basis of General valence force field (GVFF) for both in-plane and out-of-plane vibrations. The potential energy constants obtained in this study are refined using numerical methods.

Key words: FT-IR, FT-Raman, 2-amino-4,6-dimethylpyrimidine, normal coordinate analysis, potential energy distribution.

I. Introduction

A pyrimidine is a nucleotide (nucleoside + phosphate group) whose basic structure is cyclohexane with nitrogen atoms positioned at 1 and 3. This molecule is also aromatic and planar.

Pyrimidines have a long and distinguished history extending from the days of their discovery as important constituents of nucleic acids to their current use in the chemotherapy of AIDS.

During the last two decades, several pyrimidine derivatives have been developed as chemotherapeutic agents and have found wide clinical applications[1].
In the present paper, an effort has been made to record spectra and to assign the observed fundamental modes of vibrations. The evaluation of potential energy constant has been made on the basis of General Valence Force Field (GVFF) by applying wilson's FG matrix mechanism [2].

II. Experimental Details

Pure chemical of 2-amino-4,6-dimethylpyrimidine is obtained from Lancaster chemical company, England and used as such without any further purification.

The FT-IR spectrum of the title compound was recorded in the region 4000-400 cm^{-1} using KBr pellet. The Bruker IFS 66V model FT-IR spectrometer was used for the spectral measurements. The globar and mercury arc sources, KBr beam splitters are used while recording FT-IR spectrum of the title compound.

The FT-Raman spectrum was recorded on a Bruker IFS 66V model interferrometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the stokes region (4000-100cm^{-1}) using the 1064nm line of a Nd:YAG laser for excitation operating at 200mW of power.

III. Results and Discussion

3.1. Structure and symmetry

The molecular structure of 2-amino-4,6-dimethylpyrimidine is shown in Fig. 1. From the structural point of view the molecule is assumed to have C_S point group symmetry. The 48 fundamental modes of vibrations arising for this molecule are distributed into 33A′ and 15A″ species. The A′ and A″ species represent the in-plane and out-of-plane vibrations.

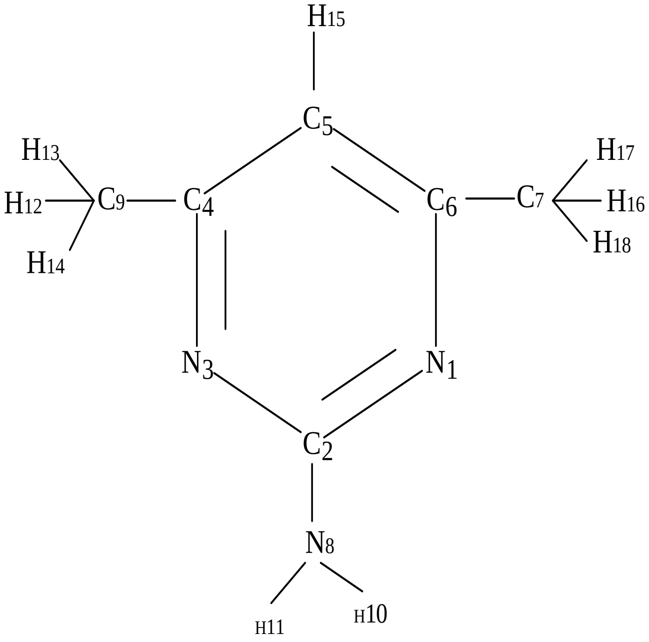

Fig 1 : Molecular structure of 2-amino-4,6-dimethylpyridine

3.2. Normal coordinate Analysis

The evaluation of potential energy constants are made on the basis of GVFF by applying wilson's FG matrix mechanism. The structural parameters were taken from the sutton's table[3]. The vibrational secular determinants have been solved using the computer programmes with the SIMPLEX optimization procedure[4]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature[5]. All the force constants have been refined via a non-linear square fit analysis between the calculated and observed frequencies. The refinement converged smoothly in three cycles.

3.3. Symmetry coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 60 standard internal valence coordinates (containing 12 redundancies) were defined in Table 1. From these a non-redundant set of local internal coordinates were constructed (Table 2) much like the natural internal coordinates recommended by IUPAC [6,7]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

Table 1: Definition of internal Coordinates of 2-amino-4,6-dimethylpyrimidine

No(i)	Symbol	Type	Definition
Stretching			
1-4	r_i	C-C	C4-C5, C5-C6, C6-C7, C4-C9
5-9	R_i	C-N	C2-N1, C2-N3, C4-N3, C6-N1, C2-N8
10	q_i	C-H	C5-H15
11-16	q_i	C-H (methyl)	C7-H16, C7-H17, C7-H18, C9-H12, C9-H13, C9-H14
17-18	P_i	N-H	N8-H10, N8-H11
In-Plane bending			
19-20	α_i	C-C-H	C6-C5-H15, C4-C5-H15
21-22	α_i	N-C-N	N3-C2-N8, N1-C2-N8
23-24	δ_i	C-C-C	C5-C6-C7, C5-C4-C9
25-26	δ_i	N-C-C	N3-C4-C9, N1-C6-C7
27-28	γ_i	C-N-H	C2-N8-H10, C2-N8-H11
29	γ_i	H-N-H	H10-N8-H11
30-35	β_i	Ring	C6-C5-C4, C5-C4-N3, C4-N3-C2, N3-C2-N1, C2-N1-C6, N1-C6-C5
36-41	θ_i	C-C-H (Methyl)	C6-C7-H16, C6-C7-H17, C6-C7-H18, C4-C9-H12, C4-C9-H13, C4-C9-H14
42-47	σ_i	H-C-H	H16-C7-H17, H16-C7-H18, H18-C7-H17, H12-C9-H13, H12-C9-H14, H14-C9-H13
Out-of-plane bending			
48	ω_i	C-H	H15-C5-C6-C4
49	ψ_i	C-N	N14-C2-N1-C3
50-51	π_i	C-C	C7-C6-N1-C5, C9-C4-N3-C5
Torsion			
52-57	t_i	τ Ring	C2-N3-C4-C5, N3-C4-C5-C6, C4-C5-C6-N1, C5-C6-N1-C2, C6-N1-C2-N3, N1-C2-N3-C4
58-59	t_i	τ C-CH_3	(C5, N1) – C6-C7- (H16,H17,H18) (C5-N3)-C4-C9-(H12,H13,H14)
60	t_i	τC-NH2	C2-N8-H11-H10

For numbering of atoms refer Fig.1.

Table 2: Definition of local symmetry coordinates of 2-amino-4,6-dimethylpyridine

No.(i)	Type	Definition
1-4	CC	r_1, r_2, r_3, r_4
5-9	CN	R_5, R_6, R_7, R_8, R_9
10	CH	q_{10}
11-12	CH_3ss	$(q_{11}+q_{12}+q_{13})/\sqrt{3}$, $(q_{14}+q_{15}+q_{16})/\sqrt{3}$
13-14	CH_3ips	$(2q_{11}-q_{12}-q_{13})/\sqrt{6}$, $(2q_{14}-q_{15}-q_{16})/\sqrt{6}$
15-16	CH_3ops	$(q_{12}-q_{13})/\sqrt{2}$, $(q_{15}-q_{16})/\sqrt{2}$

17	NH_2ss	$(P_{17}+P_{18})/\sqrt{2}$
18	NH_2ass	$(P_{17}-P_{18})/\sqrt{2}$
19	bCH	$(\alpha_{19}-\alpha_{20})/\sqrt{2}$
20	bCN	$(\alpha_{21}-\alpha_{22})/\sqrt{2}$
21-22	bCC	$(\delta_{23}-\delta_{24})/\sqrt{2}$, $(\delta_{25}-\delta_{26})/\sqrt{2}$
23	NH_2 rock	$(\gamma_{27}-\gamma_{28})/\sqrt{2}$
24	NH_2 twist	$(\gamma_{27}+\gamma_{28})/\sqrt{2}$
25	NH_2 sciss	$(2\gamma_{29}-\gamma_{27}-\gamma_{28})/\sqrt{6}$
26	Rtrigd	$(\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33}+\beta_{34}-\beta_{35})/\sqrt{6}$
27	Rsymd	$(-\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33}-\beta_{34}+2\beta_{35})/\sqrt{6}$
28	Rasymd	$(\beta_{30}-\beta_{31}+\beta_{32}-\beta_{33})/\sqrt{2}$
29-30	CH_3sb	$(-\theta_{36}-\theta_{37}-\theta_{38}+\sigma_{42}+\sigma_{43}+\sigma_{44})/\sqrt{6}$, $(-\theta_{39}-\theta_{40}-\theta_{41}+\sigma_{45}+\sigma_{46}+\sigma_{47})$
31-32	CH_3ipb	$(-\sigma_{42}-\sigma_{43}-2\sigma_{44})/\sqrt{6}$, $(-\sigma_{45}-\sigma_{46}-2\sigma_{47})/\sqrt{6}$
33-34	CH_3opb	$(\sigma_{42}-\sigma_{43})/\sqrt{2}$, $(\sigma_{45}-\sigma_{46})/\sqrt{2}$
35-36	CH_3ipr	$(2\theta_{36}-\theta_{37}-\theta_{38})/\sqrt{6}$, $(2\theta_{39}-\theta_{40}-\theta_{41})/\sqrt{6}$
37-38	CH_3opr	$(\theta_{37}-\theta_{38})/\sqrt{2}$, $(\theta_{40}-\theta_{41})/\sqrt{2}$
39	ωCH	ω_{48}
40	ψCN	ψ_{49}
41-42	πCC	π_{50}, π_{51}
43	tRtrig	$(\tau_{52}-\tau_{53}+\tau_{54}-\tau_{55}+\tau_{56}-\tau_{57})/\sqrt{6}$
44	tRsym	$(\tau_{52}-\tau_{54}+\tau_{55}-\tau_{57})/\sqrt{2}$
45	tRasy	$(-\tau_{52}+2\tau_{53}-\tau_{54}-\tau_{55}+2\tau_{56}-\tau_{57})/\sqrt{12}$
46-47	tCH_3	τ_{58}, τ_{59}
48	NH_2 wag	τ_{60}

3.4. Vibrational Band Assignments

The FT-IR and FT-Raman spectra of the title compound are shown in Figs. 2-3.

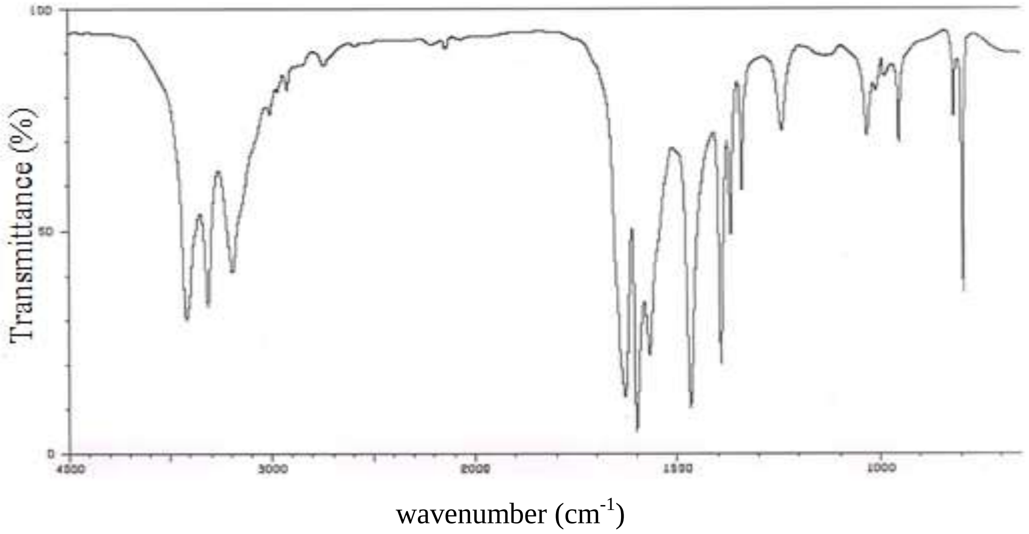

Fig 2: FT-IR spectrum of 2-amino-4,6-dimethylpyridine

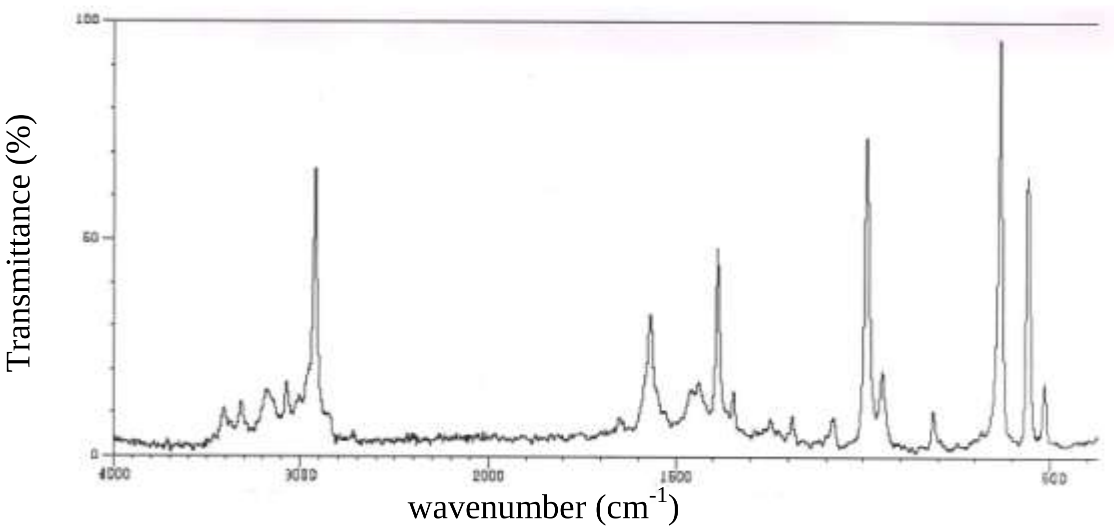

Fig 3: FT-Raman spectrum of 2-amino-4,6-dimethylpyridine

The observed frequencies of the title compound together with probable assignments, calculated frequencies and PEDS are presented in Table 3.

Table 3: Vibrational frequencies and assignments of 2-amino-4,6-dimethylpyridine

S. No.	Species	Observed frequency (cm^{-1})		Calculated Frequency (cm^{-1})	Assignment (% PED)
		FT-IR	FT-Raman		
1	A′	3312	-	3301	NH_2 ass (99)
2	A′	3191	-	3182	NH_2 ss (98)
3	A′	3006	-	2998	C-H stretching (98)
4	A′	-	2995	2985	CH_3 ips (98)
5	A′	2980	-	2968	CH_3 ips (97)
6	A′	2930	-	2920	CH_3 ss (97)
7	A′	-	2924	2915	CH_3 ss (98)
8	A′	-	2767	2756	CH_3 ops (89)
9	A′	2740	-	2730	CH_3 ops (90)
10	A′	1628	-	1619	NH_2 sciss (85)
11	A′	1600	-	1590	C-C stretching (72)
12	A′	-	1589	1577	C-C stretching (70)
13	A′	1568	-	1558	C-C stretching (71)
14	A′	-	1463	1452	CH_3 ipb (83)
15	A′	1456	-	1446	CH_3 ipb (84)
16	A′	-	1440	1429	C-C stretching (72)
17	A′	-	1423	1414	C-N stretching (75)
18	A′	1395	-	1403	C-N stretching (76)
19	A′	-	1389	1398	C-N stretching (80)
20	A′	1368	-	1378	CH_3 sb (88)
21	A′	-	1359	1367	CH_3 sb (87)
22	A′	-	1348	1357	C-N stretching (81)
23	A′	1340	-	1330	C-N stretching (79)
24	A′	1242	-	1231	C-H in-plane bending (70)
25	A″	1159	-	1150	CH_3 opb (87)
26	A″	-	1149	1139	CH_3 opb (88)
27	A′	-	1106	1116	Ring deformation in-plane bending (52)
28	A′	1032	-	1041	NH_2 rock (68)

29	A′	1009	-	1020	Ring deformation in-plane bending (51)
30	A′	-	995	1004	CH_3 ipr (79)
31	A′	989	-	998	Ring deformation in-plane bending (53)
32	A′	982	-	971	CH_3 ipr (78)
33	A″	-	959	949	CH_3 opr (77)
34	A″	950	-	939	CH_3 opr (76)
35	A′	818	-	828	C-N in-plane bending (66)
36	A′	-	810	819	C-C in-plane bending (65)
37	A″	793	-	801	C-N out-of-plane bending (59)
38	A″	638	-	628	Ring deformation out-of-plane bending (57)
39	A″	-	631	619	NH_2 wag (61)
40	A′	-	561	571	C-C in-plane bending (64)
41	A″	554	-	562	Ring deformation out-of-plane bending (58)
42	A″	545	-	535	C-H out-of-plane bending (63)
43	A″	-	514	503	Ring deformation out-of-plane bending (59)
44	A″	492	-	482	C-H out-of-plane bending (54)
45	A″	-	451	442	C-H out-of-plane bending (53)
46	A″	-	345	335	NH_2 twist (69)
47	A″	-	251	240	CH_3 torsion (57)
48	A″	-	215	206	CH_3 torsion (55)

Abbreviations used : ss – symmetric stretching; ass – antisymmetic stretching; ips- in-plane stretching; ops – out-of-plane stretching; sb-symmetic bending; ipb – in-plane bending; opb – out of-plane bending; ipr – in-plane rocking; opr-out-of-plane rocking.

3.4.1. C-H vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100cm^{-1}, which is the characteristic region for the ready identification of C-H stretching vibrations [8]. In this region the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, C-H vibration has found at 3006cm^{-1} in FT-IR.

3.4.2. C-C vibrations

The bands between 1400 and 1650cm^{-1} in benzene derivatives are due to C-C stretching vibrations [9]. Therefore, the C-C stretching vibrations of the title compound are observed at 1600, 1568cm^{-1} in IR and 1589, 1440cm^{-1} in Raman.

3.4.3. C-N vibrations

The identification of C-N stretching frequency is very difficult task, since the mixing bands are possible in this region. Hence the FT-IR bands observed at 1395, 1340cm^{-1} in IR and 1423, 1389, 1348cm^{-1} in Raman of the title compound are assigned to C-N stretching modes of vibrations. These assignments are made in accordance with the assignments proposed by krishna kumar et al.[10].

3.4.4. Amino group vibrations

According to socrates [11] the frequencies of the amino group appear around 3500-3300cm^{-1} for NH_2 stretching, 1700-1600cm^{-1} for scissoring and 1150-900cm^{-1} for rocking deformations. The antisymmetric and symmetric stretching modes of NH_2 group are found at 3312cm^{-1} and 3191cm^{-1} in IR for the title compound. The band appeared at 1628cm^{-1} in infrared is assigned unambiguously to the scissoring mode of the NH_2 group. The NH_2 rocking mode has been assigned to 1032cm^{-1} in IR. The Raman bands for wagging and twisting NH_2 modes of the title compound are identified at 631cm^{-1} and 345 cm^{-1} respectively.

3.4.5. Methyl Group vibrations

The methyl group substituted at the third position of the title compound give raise to asymmetric and symmetric stretching vibrations.

The CH_3ss frequencies are established at 2930cm^{-1} in IR, 2924cm^{-1} in Raman and CH_3ips at 2980cm^{-1} in IR, 2995cm^{-1} in Raman for the title compound.

The two in-plane methyl hydrogen deformation modes are also well established. We have observed the symmetrical methyl deformation modes CH_3sb at 1368cm^{-1} in IR, 1359cm^{-1} in Raman and in-plane bending methyl deformation modes CH_3 ipb at 1463cm^{-1} in Raman, 1456cm^{-1} in IR. The bands at 2767cm^{-1} in Raman, 2740cm^{-1} in IR and 1159cm^{-1} in IR, 1149cm^{-1} in Raman are attributed to CH_3ops and CH_3opb respectively in the A″ species. The methyl deformation modes mainly coupled with the in-plane bending vibrations.

The bands obtained at 995cm^{-1} in Raman, 982cm^{-1} in IR and 959cm^{-1} in Raman, 950cm^{-1} in IR are assigned to CH_3 in-plane and out-of-plane rocking modes. The assignments of the band 251, 215cm^{-1} in Raman are attributed to methyl twisting mode. These assignments are also supported by the literature[12].

IV. Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed for the title compound. A systematic set of symmetry coordinates have been constructed. The closer agreement obtained between the calculated and the observed frequencies and the PED calculations are also supporting the assignments made for various functional groups present in the molecule.

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