Vibrational Spectroscopic Studies of 2,6-dimethyl pyridine

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ABSTRACT

The molecular vibrations of 2,6-dimethyl pyridine was investigated by FT-IR and FT-Raman spectroscopies. Normal co-ordinate calculations of 2,6-dimethyl pyridine have been carried out using wilson's FG matrix 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.

Introduction

2,6-dimethyl pyridine or 2,6-lutidine is an organic compound, heterocyclic and aromatic, natural. It is a dimethyl substituted derivative of pyridine. It has been isolated from the basic fraction of coaltar and bone oil. 2,6-lutidine was also evaluated as a food additive because of its nutty aroma when present in very low concentrations, while pure, it has a pungent odour and harmful.

In organic synthesis, 2,6-dimethyl pyridine is widely used as a basis to fresh hindered. It is also used simply as solvent.

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 [1].

Experimental Methods

Pure chemical of 2,6-dimethyl pyridine 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 66 V 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 66 V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectrum was recorded in the stoke's region $(4000 - 100$ cm$^{-1})$ using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mW of power.

Results and Discussion

Structure and Symmetry

The molecular structure of 2,6-dimethyl pyridine is shown in Fig. 1. From the structural point of view the molecule is assumed to have C_s point group symmetry. The 45 fundamental modes of vibrations arising for this molecule are distributed into 31 A' and 14 A" species. The A' and A" species represent the in-plane and out-of-plane vibrations.
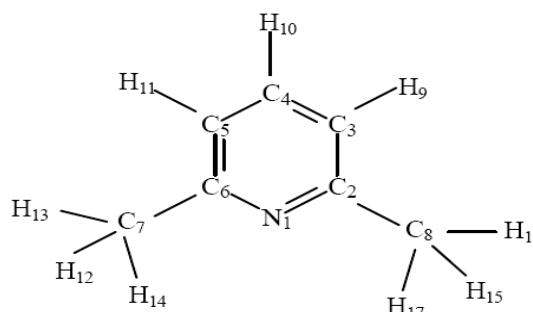

Fig 1. Molecular structure of 2,6-dimethyl pyridine

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 [2]. The vibrational secular determinants have been solved using the Computer programmes with the SIMPLEX optimization procedure [3]. The initial set of force constants and the vibrational frequencies required for the calculations were taken from the literature [4].

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.

Symmetry Coordinates

Detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, the full set of 58 standard internal valence coordinates (containing 13 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 [5,6]. Theoretically calculated force fields were transformed to the latter set of vibrational coordinates and used in all subsequent calculations.

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Table 1. Definition of internal Coordinates of 2,6-dimethyl pyridine.

No(i)	Symbol	Type	Definition
Stretching			
1-6	r_i	C–C	C2–C3, C3–C4, C4–C5, C5–C6, C2–C8, C6–C7
7-8	R_i	C–N	C2 – N1, C6–N1
9-17	q_i	C–H	C3–H9, C4–H10, C5–H11, C7–H12, C7–H13, C7–H14, C8–H15, C8–H16, C8–H17
In-plane bending			
18-23	α_i	C–C–H	C2–C3–H9, C4–C3–H9, C3–C4–H10, C5–C4–H10, C4–C5–H11, C6–C5–H11
24-25	α_i	C–C–N	C3–C2–N1, C5–C6–N1
26-31	β_i	Ring	C2–C3–C4, C3–C4–C5, C4–C5–C6, C5–C6–N1, C6–N1–C2, N1–C2–C3
32-37	θ_i	C–C–H (Methyl)	C2–C8–H15, C2–C8–H16, C2–C8–H17, C6–C7–H12, C6–C7–H13, C6–C7–H14
38-43	σ_i	H–C–H	H15–C8–H16, H15–C8–C17, H17–C8–H16, H12–C7–H14, H12–C7–H13, H13–C7–H14
44-45	α_i	C–C–C	C3–C2–C8, C5–C6–C7
Out-of-plane bending			
46-48	ω_i	C–H	H9–C3–C2–C4, H10–C4–C3–C5, H11–C5–C4–C6
49	π_i	C–C	C8–C2–N1–C3
50	ψ_i	C–N	C7–C6–C5–N1
Torsion			
51-56	t_i	τ Ring	N1–C6–C5–C4, C6–C5–C4–C3, C5–C4–C3–C2, C4–C3–C2–N1, C3–C2–N1–C6, C2–N1–C6–C5
57-58	t_i	τC–CH$_3$	(C3–N1)–C2–C8– (H15, H16, H17), (C5, N1) –C6–C7–(H12, H13, H14)

For numbering of atoms refer Fig.1.

Table 2. Definition of local symmetry coordinates of 2,6-dimethyl pyridine.

No.(i)	Type	Definition
1-6	CC	$r_1, r_2, r_3, r_4, r_5, r_6$
7-8	CN	R_7, R_8
9-17	CH	$q_9, q_{10}, q_{11}, q_{12}, q_{13}, q_{14}, q_{15}, q_{16}, q_{17}$
18-20	bCH	$(\alpha_{18} - \alpha_{19})/\sqrt{2}$, $(\alpha_{20} - \alpha_{21})/\sqrt{2}$, $(\alpha_{22} - \alpha_{23})/\sqrt{2}$
21	bCN	$(\alpha_{24} - \alpha_{25})/\sqrt{2}$
22	Rtrigd	$(\beta_{26} - \beta_{27} + \beta_{28} - \beta_{29} + \beta_{30} - \beta_{31})/\sqrt{6}$
23	Rsymd	$(-\beta_{26} - \beta_{27} + \beta_{28} - \beta_{29} - \beta_{30} + 2\beta_{31})/\sqrt{6}$
24	Rasymd	$(\beta_{26} - \beta_{27} + \beta_{28} - \beta_{29})/\sqrt{2}$
25-26	CH$_3$sb	$(-\theta_{32} - \theta_{33} - \theta_{34} + \sigma_{38} + \sigma_{39} + \sigma_{40})/\sqrt{6}$, $(-\theta_{35} - \theta_{36} - \theta_{37} + \sigma_{41} + \sigma_{42} + \sigma_{43})/\sqrt{6}$
27-28	CH$_3$ipb	$(-\sigma_{38} - \sigma_{39} - 2\sigma_{40})/\sqrt{6}$, $(-\sigma_{41} - \sigma_{42} - 2\sigma_{43})/\sqrt{6}$
29-30	CH$_3$opb	$(\sigma_{38} - \sigma_{39})/\sqrt{2}$, $(\sigma_{41} - \sigma_{42})/\sqrt{2}$
31-32	CH$_3$ipr	$(2\theta_{32} - \theta_{33} - \theta_{34})/\sqrt{6}$, $(2\theta_{35} - \theta_{36} - \theta_{37})/\sqrt{6}$
33-34	CH$_3$ opr	$(\theta_{33} - \theta_{34})/\sqrt{2}$, $(\theta_{36} - \theta_{37})/\sqrt{2}$

35	bCC	$(\alpha_{44} - \alpha_{45})/\sqrt{2}$
36-38	ωCH	$\omega_{46}, \omega_{47}, \omega_{48}$
39	πCC	π_{49}
40	ψCN	ψ_{50}
41	tRtrig	$(\tau_{51} - \tau_{52} + \tau_{53} - \tau_{54} + \tau_{55} - \tau_{56})/\sqrt{6}$
42	tRsym	$(\tau_{51} - \tau_{53} + \tau_{54} - \tau_{56})/\sqrt{2}$
43	tRasy	$(-\tau_{51} + 2\tau_{52} - \tau_{53} - \tau_{54} + 2\tau_{55} - \tau_{56})/\sqrt{12}$
44-45	tCH$_3$	τ_{57}, τ_{58}

Vibrational Band Assignments

The FT-IR and FT-Raman Spectra of the title compound are shown in Figs. 2-3.
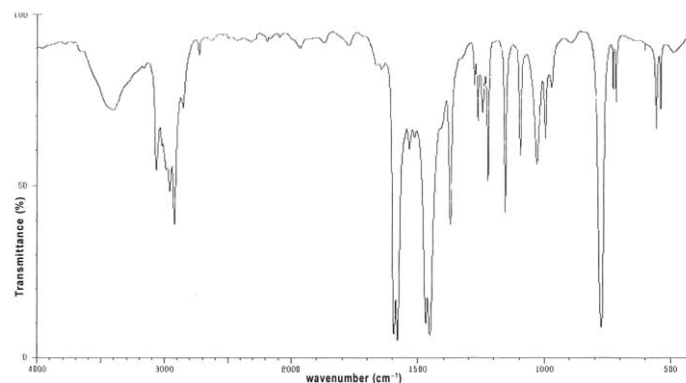
Fig 2. FT-IR spectrum of 2,6-dimethyl pyridine.
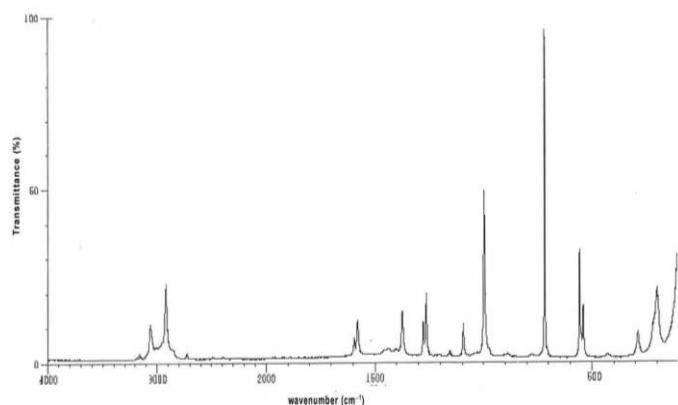
Fig 3. FT-Raman spectrum 2,6-dimethyl pyridine.

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

Table 3. Vibrational frequencies and assignments of 2,6-dimethyl pyridine.

S. No.	Species	Observed frequency (cm⁻¹)		Calculated Frequency (cm⁻¹)	Assignment (% PED)
		FT-IR	FT-Raman		
1	A′	3099	-	3088	C-H Stretching (99)
2	A′	3083	-	3074	C-H Stretching (97)
3	A′	3064	-	3054	C-H Stretching (98)
4	A′	3032	-	3024	C-H Stretching (97)
5	A′	3015	-	3006	C-H Stretching (99)

Contd...

6	A′	2985	-	2975	C-H Stretching (98)
7	A′	2968	-	2960	C-H Stretching (96)
8	A′	-	2931	2921	C-H Stretching (99)
9	A′	2923	-	2912	C-H Stretching (96)
10	A′	-	1680	1672	C-C Stretching (72)
11	A′	1644	-	1634	C-C Stretching (70)
12	A′	1594	-	1585	C-C Stretching (71)
13	A′	1581	-	1571	C-C Stretching (72)
14	A′	1534	-	1523	C-C Stretching (71)
15	A′	1514	-	1506	C-C Stretching (70)
16	A′	1469	-	1477	CH$_3$ ipb (84)
17	A′	1462	-	1472	C-N Stretching (76)
18	A′	-	1451	1460	CH$_3$ ipb (83)
19	A′	-	1423	1431	C-N Stretching (75)
20	A′	-	1378	1387	CH$_3$ sb (88)
21	A′	1372	-	1380	CH$_3$ sb (87)
22	A′	1278	-	1269	C-H in-plane bending (70)
23	A′	1264	-	1254	C-H in-plane bending (72)
24	A′	1246	-	1235	C-H in-plane bending (71)
25	A′	1224	-	1214	Ring deformation in-plane bending (52)
26	A′	-	1205	1196	C-N in-plane bending (66)
27	A″	1158	-	1167	CH$_3$ opb (87)
28	A″	-	1151	1143	CH3 opb (88)
29	A′	-	1096	1086	Ring deformation in-plane bending (53)
30	A′	1090	-	1079	Ring deformation in-plane bending (51)
31	A′	1031	-	1023	CH$_3$ ipr (79)
32	A′	-	1005	996	CH$_3$ ipr (78)
33	A″	997	-	986	CH$_3$ opr (76)
25	A′	1224	-	1214	Ring deformation in-plane bending (52)
26	A′	-	1205	1196	C-N in-plane bending (66)
27	A″	1158	-	1167	CH$_3$ opb (87)
28	A″	-	1151	1143	CH3 opb (88)
29	A′	-	1096	1086	Ring deformation in-plane bending (53)
30	A′	1090	-	1079	Ring deformation in-plane bending (51)
31	A′	1031	-	1023	CH$_3$ ipr (79)
32	A′	-	1005	996	CH$_3$ ipr (78)
33	A″	997	-	986	CH$_3$ opr (76)
34	A″	971	-	962	CH$_3$ opr (77)
35	A″	774	-	784	C-H out-of-plane bending (64)
36	A″	729	-	738	C-H out-of-plane bending (63)
37	A″	717	-	725	C-N out-of-plane bending (59)
38	A″	-	641	650	Ring deformation out-of-plane bending (57)
39	A″	602	-	613	Ring deformation out-of-plane bending(58)
40	A′	-	578	568	C-C in-plane bending (65)
41	A″	567	-	558	Ring deformation out-of-plane bending(59)

42	A″	540	-	548	C-H out-of-plane bending (60)
43	A″	469	-	478	CH$_3$ torsion (57)
44	A″	-	433	444	CH$_3$ torsion (55)
45	A″	-	203	212	C-C out-of-plane bending (54)

Abbreviations used : Sb – symmetric bending; ipb – in – plane bending; opb –out –of–plane; bending; ipr – in – plane rocking; opr – out – of – plane rocking

C-H Vibrations

The molecular structure shows the presence of C-H stretching vibrations in the region 3000-3100 cm^{-1} which is the characteristic region for the ready identification of C-H stretching vibrations [7,8]. In this region the bands are not affected appreciably by the nature of the substituents. Hence, in the present investigation, C-H vibrations have found at 3099, 3083, 3064, 3032, 3015, 2985, 2968, 2923 cm^{-1} in IR and 2931 cm^{-1} in Raman.

C-C Vibrations

The bands between 1400 and 1650 cm^{-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 1644, 1594, 1581, 1534, 1514 cm^{-1} in IR and 1680 cm^{-1} in Raman.

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 band observed at 1462 cm^{-1} in IR and 1423 cm^{-1} in Raman of the title compound is assigned to C-N stretching modes of vibration. These assignments are made in accordance with the assignments proposed by Krishnakumar et al. [10].

Methyl Group Vibrations

The methyl group substituted at the first position of the title compound given raise to asymmetric and symmetric stretching vibrations. We have observed the symmetrical methyl deformation modes CH3sb at 1372 cm^{-1} in IR and 1378 cm^{-1} in Raman and in-plane bending methyl deformation modes CH3ipb at 1469 cm^{-1} in IR and 1451 cm^{-1} in Raman. The bands at 1158 cm^{-1} in IR and 1151 cm^{-1} in Raman are attributed to CH3opb in the A" species. The bands obtained at 1031 cm^{-1} in IR and 1005 cm^{-1} in Raman and 997, 971 cm^{-1} in IR are assigned to CH3 in-plane and out-of- plane rocking modes. These assignments are also supported by the literature [11].

Conclusion

Based on the normal coordinate analysis a complete vibrational analysis was performed on 2,6-dimethyl pyridine. A systematic set of symmetric 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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