

Spectroscopic Studies of Substituted Methyl-Hydroxy-Pyridine

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ABSTRACT

N-Heterocyclic molecules like pyridine, pyrimidine, cytosine, uracil etc. and their derivatives are of immense importance as they play a central role in the structure and properties of the biologically important nucleic acids. the pyridine ring system is very important as a structural unit in the natural products and compounds of pharmaceutical interest. In view of it, the laser Raman and infrared absorption spectra of 3-cyano-4,6-dimethyl-2-hydroxy pyridine have been reported. The bands observed are discussed assuming the molecule C_s point group symmetry.

Key Words: infrared a laser Raman spectra

INTRODUCTION

N-Heterocyclic molecules like pyridine, pyrimidine, cytosine, uracil etc. and their derivatives are of immense importance as they play a central role in the structure and properties of the biologically important nucleic acids. the pyridine ring system is very important as a structural unit in the natural products and compounds of pharmaceutical interest. It has been shown by Jesson et al[1] that pyridine molecule has planar structure in the ground state and quasi planar one in the excited state. Kaya, Mochizuki and Ito[2] have reported the systematic study of the electronic absorption and Raman spectra of pyridine and its derivatives. Major part of the work on pyridine regarding the spectral studies was tabulated by Wilmshurst, Bernstein[3], Innes and co-workers [4]. Many workers [5,6] also studied the vibrational spectra of biologically important pyridine derivatives through the high complexity and low symmetry of these molecules have made the interpretation extremely difficult. R.K Goel [7,8], S.Mohan[9], Medi [10], Srivastava [11], Tripathi & Pandey [12], Gupta et al [13], Baruah et al [14] and Panday [15] have reported the appropriate study regarding pyridine and its derivatives.

Several workers [16,17] have shown the investigations for few Cyano substituted pyridine and substituted benzonitriles which constitutes the basis of this discussion.

The objective of the investigations under study is to identify the IR and Raman frequencies corresponding to the substituents as well as to the ring fundamentals and their correlations with similar molecules.

Considering the Cyano group as a single mass point, the interpretation of this molecule under consideration is made by assuming the C_s point group symmetry. Much help have been taken from the work similar to pyridine and their derivatives.

In view of the above discussion, the present chapter reports the vibrational spectra, ultraviolet spectra in different solvents and thermodynamic constants of the 3-cyano-4,6-dimethyl-2-hydroxy pyridine is reported and discussed.

Experimental

The infrared spectra of Specpure grade sample 3-cyano-4,6-dimethyl-2-hydroxy pyridine (hereafter referred as 3,4,6,2-CDMHP) is recorded region in the 400-4000 cm^{-1} on Perkin Elmer Spectrophotometer model 52 using KBr pellet techniques. The laser Raman spectra of said molecule has been recorded in the region 200-4000 cm^{-1} on Spex Rama lab spectrophotometer using 52 MW argon krypton laser beam of wavelength 488 nm. The frequencies of all the sharp bands are accurate to $\pm 1 \text{ cm}^{-1}$

RESULTS AND DISCUSSION:

The observed frequencies of recorded spectra with probable assignments of the molecule are given in Table 1. The C_s point group symmetry has been assumed for this molecule.

VIBRATIONAL SPECTRA

C-H VIBRATIONS: The nitrogen atom of pyridine is isoelectric with the CH group. As there is little difference in mass or in the bond strengths to adjacent atoms. It is to be expected that the majority of the fundamental frequencies will be very close to those of benzene and the difference will only arise due to substituent's attached to the ring [18].

Since the molecule 3,4,6,2-CDMHP is tetra-substituted pyridine, therefore only one (C-H) valence oscillation is expected. According to Bellamy [17] and other [18], this (C-H) stretching mode lies in the region 3000-3100 cm^{-1} (KBr) has been assigned to (C-H) stretching mode.

Sanyal et al [19] have assigned C-H in plane bending and out-of-plane bending modes at 940 and 848 cm^{-1} respectively in 4,6-dihydroxy-2methyl pyrimidine. The IR band at 948 cm^{-1} (KBr) has been assigned to C-H in plane bending vibration while the Raman band at 842 cm^{-1} has assigned to C-H out-of-banding vibration, which find support from the literature value [11,17].

From the available in N-heterocyclicmolecule [20] the IR band observed at 3144 cm^{-1} (KBr) in the molecule 3,4,6,2-CDMHP may be assigned to N-H stretching mode. This is possible only when there is a proton migration from the ring. It can be infrared that in the said molecule, proton migration takes place from hydroxyl group to the nitrogen of the ring, giving rise to N-H stretching mode. The IR band at 1670 cm^{-1} (KBr) has been assigned to (N-H) in plane bending mode which finds support from the literature [13,20] while the IR band observed at 846 cm^{-1} (KBr) has been assigned to N-H out-of-plane bending vibration mode.

C-C VIBRATIONS: In pyridine and its derivatives the frequency of ring breathing mode has been assigned in the region 690-884 cm^{-1} [17,19-21]. The Raman band observed at 743 cm^{-1} (KBr) has been assigned to this mode. According to Rao [21], the (C-C) stretching frequency in pyridine and its related compounds has been observed in the region (1320-1630). Therefore, the IR bands observed at 1418, 1567 and 1643 cm^{-1} (KBr) have been assigned to this mode. The ring in-plane and out-of-plane bending modes are well assigned as given in Table 1 in their respective region [22-24]. The IR band observed at 1014 cm^{-1} assigned to C-C-C in plane bending mode while the Raman band observed at 467 cm^{-1} is assigned as C-C-C out-of-plane bending mode [8].

C-N VIBRATIONS: Some workers [9] assigned (C-N) stretching mode at 1340 cm^{-1} in unsubstituted benzene. Goel et al [7] have assigned this mode at 1395 cm^{-1} in case of 2-choloro pyridine. In the present study the IR band observed at 1358 cm^{-1} (KBr) has taken to represent this mode.

C-X VIBRATIONS: Some workers [25] have assigned (C-OH) stretching mode around 1300 cm^{-1} in substituted benzenes. Gupta et al [26] have assigned this mode at 1262, 1265 and 1270 cm^{-1} in hydroxyl methoxy benzaldehyde while Vipin et al [27] have assigned this mode

at 1270 cm^{-1} in identical compound. In view of these assignments the IR band observed at 1242 cm^{-1} (KBr) has been assigned to this mode.

The (C-OH) in-plane bending mode has been assigned at IR band at 558 cm^{-1} KBr with the corresponding Raman band at 545 cm^{-1} in the said molecule. The out-of-plane bending mode has been identified at 286 cm^{-1} in Raman spectrum. These assignments also find support from the literature value [28].

In present molecule, H-atom of hydroxy group migrates to N-atom of the ring due to tautomerism behavior and give (C=O) mode. The (C=O) stretching frequency has been assigned at IR band 1670 cm^{-1} (in KBr) while the (C=O) in plane bending and out-of-plane bending have been assigned at IR band 528 cm^{-1} respectively. These assignments are in accordance with the literature value [13].

The molecule 3,4,6,2-CDMHP has two methyl groups at 4 and 6 positions, hence two C-CH₃ valence oscillations are expected. It has been shown by Colthup [22] that the C-CH₃ stretching vibrations appear in the range $1200\text{--}1300\text{ cm}^{-1}$. In view of this, the IR band observed at 1159 and 1242 cm^{-1} have been assigned to C-CH₃ stretching modes in the said molecule. The Raman band observed at 569 cm^{-1} have been assigned to (C-CH₃) in-plane bending modes, while only one (C-CH₃) out-of-plane bending mode is observed in the present molecule which has been assigned at Raman band 300 cm^{-1} . These assignments, also find support from the literature value [19,29].

GROUP VIBRATIONS

-OH GROUP : For the molecules containing a hydroxyl group, the O-H valence oscillation appears in the region $3500\text{--}3700\text{ cm}^{-1}$ [17]. Gupta et al [13] have assigned O-H stretching mode at 3430 cm^{-1} in substituted pyridines. Some workers [28] has reported the O-H stretching mode in the region $3145\text{--}3430\text{ cm}^{-1}$. In view of these, the IR band observed at 3427 cm^{-1} (KBr) has been taken to represent O-H stretching mode while the Raman band observed at 317 cm^{-1} has been assigned to (O-H) out of plane bending mode which find support from the literature [13].

The spectra of substituted benzene show the O-H torsion mode as usually a weak band [21]. Green et al [30] and Others [22-24] have assigned this mode near 420 cm^{-1} in pentachloro phenols. During the present investigation, this mode has been identified at 450 cm^{-1} (KBr) with the counterpart Raman value at 450 cm^{-1} .

-CH₃Group: Bellamy [17] have examined a large number of hydrocarbons containing methyl groups and found that in all the cases two strong band occurs at 2962 and 2872 cm⁻¹ corresponding to asymmetric and symmetric stretching modes of methyl group. Goel et al [8] have assigned the CH₃ asymmetric stretching modes at 3029, 2944, 2951 and 2884 cm⁻¹ while symmetric stretching modes of methyl groups at 2829 and 2804 cm⁻¹ in 5,6-dimethyl uracil. In view of this, the IR bands observed at 2799 and 2848 cm⁻¹ have been assigned as CH₃ asymmetric stretching mode in the present molecule.

The symmetrical deformation mode of hydrogen atoms of a methyl group results in an absorption band in the range 1385-1370 cm⁻¹ which is extremely stable in position provides that the methyl group is attached to another carbon atom [21,22]. Bellamy [17] also suggested the range 1450±20 cm⁻¹ for asymmetric deformation mode of methyl group. Goel et al [8] have assigned the bands at 1518, 1500, 1475 and 1460 cm⁻¹ to CH₃ symmetric deformation mode in 4,6-dimethyl pyrimidine. In view of these assignments, the IR bands observed at 1358 and 1400 cm⁻¹ have been assigned to CH₃ symmetric deformation mode while the bands observed at 1466 and 1518 cm⁻¹ (KBr) have been assigned to CH₃ asymmetric deformation modes. It also finds support from the literature [27] have assigned these modes at 1030 cm⁻¹ and 1050 cm⁻¹ in 2,4-dimethyl-6-hydroxy pyrimidine while Ahmad et al [31] have assigned these modes at 1040 and 1065 cm⁻¹ in 4-amino-2,6-dimethyl pyrimidine. In view of these, the IR band observed at 1014, 1046 and 1078 cm⁻¹ have been assigned to this mode. The band observed at 220, 195 and 185 cm⁻¹ have been assigned to CH₃ torsion modes in 4-amino-2,6-dimethyl pyrimidine [31]. In view of the above, the Raman bands observed at 225 and 249 cm⁻¹ have assigned to CH₃ torsional modes in 3,4,6,2-CDNHP.

-CN Group: Some workers [32] on nitriles show, that the infrared absorptions appears on the region 2300-2200 cm⁻¹. These investigator shows that for the aromatic compound in which the CN group was directly attached to the ring absorbed in the region 2240-2221 cm⁻¹.

Aromatic nitriles show large intensity variations in the infrared spectra but the band is always strong. According to Bellamy [17] the CN stretching for aromatic compounds appears in the region 2240-2221 cm⁻¹. Medhi and Sharma [16] assigned the band at 2240 cm⁻¹ in IR spectrum and at 2237 cm⁻¹ in the Raman spectrum to CN stretching vibration for 4-cyano pyridine. In the present investigation, the medium strong band which appears at 2230 cm⁻¹ (KBr) has been assigned to CN stretching vibrations.

Jacobson [33] noted that a band always appeared between 380 and 480 cm^{-1} in the spectra of aromatic nitrite compounds. Jacobson [33] further established that it belongs to the in-plane-bending vibration of the CN group. Medhi et al[16] assigned the band at 368 cm^{-1} in IR spectrum and at 370 cm^{-1} in Raman spectra to in-plane bending vibrations for 4-cyanopyridine. So the band observed at 385 cm^{-1} in the Raman spectrum has been assigned to this mode in the present molecule.

Jacobson[33] assigned out-of-plane CN bending mode at 170 cm^{-1} in the Raman spectra for aromatic nitrile. But in the said molecule, this, mode could not be found, due to the low frequency range.

TABLE 1

ASSIGNMENT OF VIBRATIONAL FREQUENCIES (in cm^{-1}) OF 3,4,6,2-CDMHP

Raman	IR	Assignments
225 MS	-	CH ₃ Torsion
249 MS	-	CH ₃ Torsion
286 BS	-	γ (C-OH)
300 MS	-	γ(C-CH ₃)
317 MS	-	γ (O-H)
328 W	-	γ Ring
385 MS	-	β (C-N), γ(C=O), β(C-CH ₃)
450W	450VW	(O-H) Torsion
467W	-	γ(C-C-C) Trigonal bending
-	496MS	γ Ring
520W	528W	γ Ring, β(C=O)
545W	558W	β(C-OH)
569W	-	β(C-CH ₃)
624 VW	632 MS	β Ring
638 VW	651 MS	β Ring
735 W	734 MS	γ Ring
743W	-	Ring Breathing
-	799 MS	β Ring
824 W	-	γ (C-H)

-	864 MS	Υ (N-H)
-	948 MS	β (C-H), CH ₃ rocking
-	1014 W	β (C-C-C) Trigonal bending, CH ₃ Rocking
-	1046 W	CH ₃ Rocking
-	1078 W	CH ₃ Rocking
-	1159 MS	ν (C-CH ₃), β (O-H)
-	1242 MS	ν (C-OH), ν (C-CH ₃)
-	1358 MS	ν Ring, CH ₃ sym def.
-	1400 MS	CH ₃ sym def
-	1418 MS	ν Ring
-	1466 W	CH ₃ asym def.
-	1518 MS	CH ₃ asym def.
-	1567 MS	ν ring
-	1643 S	ν ring
-	1670 S	β (N-H), ν (C=O)
-	1822 W	-
-	2230 MS	ν (C-N)
-	2799 W	ν (CH ₃) sym.
-	2848 W	ν (CH ₃) sym
-	3011 W	ν (C-H), ν (CH ₃)asym.
-	3144 W	ν (N-H)
-	3300 VW	ν (N-H) sym.
-	3427 MS	ν (N-H) asym, ν (O-H)

Where ν =Stretching, β = in-plane bending, Υ = out-of-plane bending
 Sym.=symmetric Asym.=Asymmetric Def.=Deformation
 S=Strong BS=Broad strong W=Weak
 VW=Very weak

REFERENCES

- 1) Jesson, Kroto and Ramsay, J.Chem. Phys. (U.S.A), **56** (1972) 6257.
- 2) Kaya, Mochizuki and Ito, J.Chem. Phys. (U.S.A), **65**(1976) 4163.
- 3) Wilmschurst and Bernstein, Can. J. Chem., **35**(1975)1183.
- 4) Innes, Byrne and Ross, J. Mol. Spectrosc., **22**(1967)125.

- 5) Goldstein, Mooney, Anderson and Gebbie, Spectrochim. Acta.,**21**(1965)105.
- 6) Dilella and Stidham, J. Raman Spectrosc.,**9**(1980).
- 7) R.K. Goel, S.K. Sharma and S.N. Sharma, Indian J. Pure & Appl. Phys., **18**(1980)928.
- 8) R.K. Goel, S.K. Gupta, M.L. Agarwal, and S.N. Sharma, Indian J. Pure & Appl. Phys., **19**(1981)501.
- 9) S.Mohan and V.Illangovan, Proc. Nat. Acad. Sci.(India), **65(A)**(1995)111.
- 10) K.C.Medhi and M.K.Sharma, Indian J.Phys., **66(B)**(1992)59.
- 11) S.L.Srivastava and Rohitashava, J.De. Chemie. Physiq., **75(F)**(1978)64.
- 12) G.N.R. Tripathi and S.R.Tripathi, Spectrosc Letters,**9(II)** (1976)789.
- 13) S.P. Gupta, R.K. Goel and C. Gupta, Indian J. Phys., **23**(1985)344.
- 14) G.D. Barauh, R.A. Amma, P.S. Dube and S.N. Rai, Indian J Pure & Appl Phys, **8**(1970)761.
- 15) M.R. Panday and V.V. Bhujle, Indian J Pure & Appl Phys, **8**(1970)479.
- 16) K.C. Medhi and M.K. Sharma, Indian J. Phys., **64(B)(4)**(1990)307.
- 17) L.J. Bellamy, "The Infrared Spectra of Complex Molecules", (Chapmen and Hall, London) (1975).
- 18) Kline and Turkevitch, J. Chem. Phys., **12**(1944)300.
- 19) N.K. Sanyal, R.K. Goel, K. P. Kansal and S.N. Sharma, Indian J Pure & Appl Phys, **18**(1979)1032.
- 20) Vir Singh, Seema, B.S. Yadav and Subhash Chand, Indian J Phys, **71(B)**(1997)69.
- 21) C.N.R. Rao, "Chemical Applications of Infrared Spectroscopy", (Academic Press, New York)(1963).
- 22) N.B. Colthup, L.H. Daily and S.E. Wiberly, "Introduction to IR and Raman Spectroscopy" (Academic Press Inc, New York)(1964).
- 23) Dollish, Fateley and Bentley, "Characteristic Raman Frequencies of Organic Compound", (John Willey & Sons, New York)(1974).
- 24) G. Varsanyi, "Vibrational Spectra of Benzene Derivatives", (Academic Press, New York)(1969).
- 25) B.S. Yadav, Vir Singh, Vipin Kumar and M.K. Yadav, Asian J. of Chem., **9(3)**(1997)372.
- 26) S.P. Gupta, C. Gupta, S. Sharma and R.K. Goel, Indian J. of Pure and Appl Phys., **24**(1986)111.
- 27) Vipin Kumar and Subhash Chandra, Wutan Hutan Jisuan Jishu Journal, **XVII(II)** (2021)357.

- 28) B.S. Yadav, Vipin Kumar, Vir Singh and B.S. Semwal, Indian J Pure & Appl Phys, **37**(1999)34.
- 29) Vipin Kumar and Subhash Chandra, Vidyabharati International Interdisciplinary ResearchJournal, **Oct** (2021)375.
- 30) J.H.S. Green, D.J. Harrision and W. Kynaston, Spectrochem Acta, **27**(1971)2199.
- 31) Salik Ahmed, S.D. Sharma and M. Ishaq, Spectrochim Acta, **52(A)** (1996)1369.
- 32) Holmstedt and Larsson, Acta Chem. S. Chand, **5**(1951)1179.
- 33) R.J. Jacobson and F.F. Bently, Appl Spect.,**18**(1964)88.