Vibrational Spectra Of Tri Substituted Pyridine,

N-Heterocyclic Molecule Of Biological Interest

Vipin Kumar¹, Mohit Kumar² & Ajay Kumar²

¹Dept. of Physics, SKD University, Hanumangarh (INDIA)
²Research Scholar at Deptt. of Physics, SKD University, Hanumangarh (INDIA)

Abstract: The Aromatic compounds are of great Biological importance as they play an important role in the structure and properties of nucleic acid. Further when the N-heterocyclic molecules have some substituent like-OH, -SH and -NH₂, may cause Tautomerism. The Infrared Absorption Spectra of 5-bromo-2-3-dihydroxy pyridine have been recorded. The bands observed in the IR spectra are discussed by assuming the compound under Cs point group symmetry.

Introduction

The aromatic compounds like benzene like benzaldehyde, pyridine, pyrimidine, uracil, cytosine and their derivatives are of great biological importance as they play an important role in the structure and properties of nucleic acid [1-2]. However due to their great complexity and low symmetry only a little spectral studied by some workers [3-5]. The Vibrational spectra of Di-substituted pyridines have also been studied [6-7], but very little work appears on the IR spectra of tri-substituted pyridines [8]. Further when the N-heterocyclic molecules have some substituent like-OH, -SH and -NH₂, may cause Tautomerism. Tripathi [9] have studied the vibrational and electronic spectra of some substituted pyridine; Medhi [10] studied the IR and Raman spectra of 3-hydroxy pyridine. Some workers [11-12] have also studied the electronic spectra of pyridines and substituted pyridines. In view of these the present Paper reports the vibrational spectra, ultraviolet absorption spectra and thermodynamic functions of 5-bromo-2-3-dihydroxy pyridine.

Experimental

The infrared absorption spectra of 5-bromo-2,3-dihydroxy pyridine (hereafter referred as 5,2,3-BDHP) was recorded on Perkin Elmer spectrophotometer model-52 in the region 400–4000 cm⁻¹ using KBr pellets techniques. The chemicals used were of spectroscopic grade.

Result and Discussion

The structural formula of the compound 5,2,3-BDHP is given in Figure 1.

![FIGURE: 1 MOLECULAR STRUCTURE OF 5,2,3-BDHP](image)

The IR spectra of 5,2,3-BDHP in KBr pellets is given in Figure 2. The fundamental vibrational frequencies of the said molecule are given in Table 1. The Cs Point group symmetry has been assumed for the analysis of the said molecule.

VIBRATIONAL SPECTRA
RING VIBRATIONS
C-H VIBRATIONS

Since the molecule 5,2,3-BDHP is a tri-substituted pyridinetherefore it has two hydrogen atoms left around the ring. Thus, the compound 5,2,3-BDHP may have two C-H valence oscillations which usually lies in the region 3000-3100cm⁻¹ [13]. Two IR bands have been observed at 3105cm⁻¹ (KBr) and 3115 cm⁻¹ (KBr) which are been assigned to this mode. These assignments are also in the agreement with the literature value [14,15]. Rao [16] has suggested C-H in-planeand out-of-plane bonding modes lie in the region 1000-1250cm⁻¹ respectively. Gupta et al [17] have assigned C-H in-plane bending in 4-hydroxy-4-methoxy bending mode at 1245 cm⁻¹ in 3-amino-2-chloro pyridine. Tripathi et al [8] have assigned these modes in the region 1015-1180 cm⁻¹ and 805-895cm⁻¹ in hydroxy pyridine.

In view of these assignments the bands observed at 1110 cm⁻¹ (KBr) and 1180 cm⁻¹ (KBr) have been taken to represent C-H in-plane bending while the bands observed 815 cm⁻¹ (KBr) and 850 cm⁻¹ (KBr) have been taken to represent C-H out-of-plane bending modes. These assignments are also in the agreement with literature value [18-20].
C-C, C-N AND N-H VIBRATIONS:

In benzene and substituted benzene the frequency of ring breathing mode have been assigned in the region 690-844 cm\(^{-1}\) [21,22]. The IR band observed at 785 cm\(^{-1}\) (KBr) has been assigned to ring breathing mode in the present investigation. The C-C stretching, in-plane and out-of-plane bending modes have been assigned in their respective regions [21,22] (see Table 1). The C-C-C trigonal bending vibrations have been assignment with the literature value [15,16,21].

Due to the tautomeric behaviour of the molecule, the N-H stretching frequency may appear in the molecule. Vir Singh et al. [2] have assigned this mode at 3230 cm\(^{-1}\) in 2,4-dihydroxy-6-methyl pyrimidine. In view of this assignment a weak IR band observed at 3270 cm\(^{-1}\) has been assigned to N-H in-plane bending mode of vibration while the band observed at 1680 cm\(^{-1}\) (KBr) has been assigned to N-H in-plane bending mode of vibration. This also find support from the literature [7]. Various other modes have also assigned in Table 1 in their respective regions [22].

C-X VIBRATIONS

Some workers [23] have assigned (C-OH) Stretching mode around 1300 cm\(^{-1}\) in substituted benzene. Gupta et al [17] have assigned this mode at 1262, 1265 and 1270 cm\(^{-1}\) in hydroxy methoxy benzaldehyde while Yadav et al [24] have assigned this mode at 1270 cm\(^{-1}\) in the identical compound.

In view of these assignments the bands observed at 1310 cm\(^{-1}\) (KBr) and 1345 cm\(^{-1}\) (KBr) have been assigned to this mode. The (C-OH)-in-plane bending modes have been assigned at 570 cm\(^{-1}\) (KBr) and 680 cm\(^{-1}\) (KBr) in the compound 5,2,3-BDHP.

Goel et al [12] have assigned (C-Br) stretching mode at 1065 and 1055 cm\(^{-1}\) in 3-amino-2-chloro pyridine and in 5-chloro-2,4-dimethoxy aniline. In view of these assignments, the band observed at 960 cm\(^{-1}\) (KBr) has been taken to represent (C-Br) stretching mode in 5,2,3-BDHP. The in-plane bending and out-of-plane bending mode lies in the low frequency range so these modes could not be found in the said molecule.

Since the compound is a hydroxy substituted pyridine, so the hydrogen atom of the hydroxy group at position 2 migrates to the N-atom in ring which shows the existence of C=O, N-H stretching and bondings modes. Vir Singh et al [2] have assigned a medium strong band at 1700 cm\(^{-1}\) in 2,4-dimethyl-6-hydroxy pyrimidine to represent (C=O) stretching mode of vibration and (C=O) in-plane and out-of-plane bending mode at 530 and 360 cm\(^{-1}\) in the same molecule. In view of this, the strong IR band at 1680 cm\(^{-1}\) has been assigned as (C=O) stretching mode of vibrations, while the IR band observed at 570 cm\(^{-1}\) has been assigned as(C=O) in-plane bending mode of vibration. Both the bands are taken in KBr pallet techniques.

GROUP VIBRATIONS

-OHGROUPS

In monomeric phenol [25] the -OH stretching mode appears around 3600 cm\(^{-1}\) whereas in associated species [17] it is reported in the region3145-3430 cm\(^{-1}\). Goel et al [26] have assigned this mode at 3560 cm\(^{-1}\) in 4,6-dihydroxy-2-mercapto pyrimidine.

In view of these assignments the bands observed at 3115 cm\(^{-1}\) (KBr) and 3240 cm\(^{-1}\) (KBr) have been taken to represent O-H stretching modes. The spectra of substituted benzene shows, the O-H torsion mode as usually a weak band [16]. Green et al [27] and Siquenza et al [28] have assigned this mode near 420 cm\(^{-1}\) in penta chloro phenols, while Faniran [29] have assigned this mode at 314 and 318 cm\(^{-1}\) in penta-bromo and penta-chloro-phenols. During the present investigation, these modes have been identified at 435 cm\(^{-1}\). The various other modes of this group are assigned in their own region in the Table 1[15-16].
# TABLE 1
Assignment of Vibrational Frequencies in (cm\(^{-1}\)) of 5,2,3-BDHP

<table>
<thead>
<tr>
<th>IR</th>
<th>ASSIGNMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>435 vw</td>
<td>(O-H) torsion, ring</td>
</tr>
<tr>
<td>525 w</td>
<td>ring</td>
</tr>
<tr>
<td>570 ms</td>
<td>(C=O), (C-OH)</td>
</tr>
<tr>
<td>630 w</td>
<td>ring</td>
</tr>
<tr>
<td>680 ms</td>
<td>(C-OH)</td>
</tr>
<tr>
<td>785 w</td>
<td>ring breathing, C-N-C bending vibration</td>
</tr>
<tr>
<td>815 w</td>
<td>(C-H)</td>
</tr>
<tr>
<td>850 ms</td>
<td>(C-H), (C-C-C) trigonal bending</td>
</tr>
<tr>
<td>905 w</td>
<td>(C-C-C) trigonal bending</td>
</tr>
<tr>
<td>960 ms (I)</td>
<td>(C-C-C) trigonal bending, C-Br</td>
</tr>
<tr>
<td>1110 w</td>
<td>(C-H)</td>
</tr>
<tr>
<td>1180 s</td>
<td>(C-H)</td>
</tr>
<tr>
<td>1310 s</td>
<td>(C-OH)</td>
</tr>
<tr>
<td>1345 s</td>
<td>(C-OH)</td>
</tr>
<tr>
<td>1430 ms</td>
<td>ring</td>
</tr>
<tr>
<td>1455 ms</td>
<td>ring</td>
</tr>
<tr>
<td>1575 s</td>
<td>ring</td>
</tr>
<tr>
<td>1615 s</td>
<td>ring</td>
</tr>
<tr>
<td>1680 s</td>
<td>(C=O), (N-H)</td>
</tr>
<tr>
<td>3105 vw</td>
<td>(C-H)</td>
</tr>
<tr>
<td>3115 vw</td>
<td>(C-H), (O-H)</td>
</tr>
<tr>
<td>3240 w</td>
<td>(O-H)</td>
</tr>
<tr>
<td>3270 vw</td>
<td>sym (N-H)</td>
</tr>
</tbody>
</table>

Where: □ - stretching, vw - very weak
□ - in-plane bending  w - weak
□ - out-of-plane bending  ms - medium strong
□ sym - symmetric stretching  s - strong.
REFERENCES