

INFRARED ABSORPTION SPECTRA OF 5-BROMO-2-3-DIHYDROXY PYRIDINE

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ABSTRACT

The infrared absorption spectra of 5-bromo-2-3-dihydroxy pyridine have been reported. The infrared absorption spectra of this molecule have been recorded by using KBr pellets Technique. The paper discusses bands observed in the IR spectra by assuming the compound under Cs point group symmetry.

Keywords: benzene, 5-bromo-2-3-dihydroxy pyridine, vibrational spectra,

INTRODUCTION

The aromatic compounds of the benzene family 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 greater complexity and low symmetry, only a little spectral has been studied by researchers. [3-4]. The vibrational spectra of di-substituted pyridines have also been studied [5], but very little work appears on the IR spectra of tri-substituted pyridines [6]. Further, the N-heterocyclic molecules have some substituent like-OH, -SH and -NH₂. They may cause tautomerism. *Tripathi et al.* [7] have studied the vibrational and electronic spectra of some substituted pyridine; *Medhi* [8] studied the IR and Raman spectra of 3-hydroxy pyridine. Some researchers [9-11] have also studied the electronic spectra of pyridines and substituted pyridines. In view of these, the present paper will focus on the vibrational spectra, of 5-bromo-2-3-dihydroxy pyridine.

EXPERIMENTAL

Specpure grade chemical 5-bromo-2,3-dihydroxy pyridine was obtained from M/S Aldrich Chemise, West Germany and used as such. This chemical here-after will be referred as 5,2,3-BDHP. The purity of the said compound was also confirmed by elemental analysis and melting point determination. The infrared absorption spectra of 5,2,3-BDHP was recorded on Perkin Elmer spectrophotometer model-52 in the region 400-4000 cm⁻¹ using KBr pellets techniques.

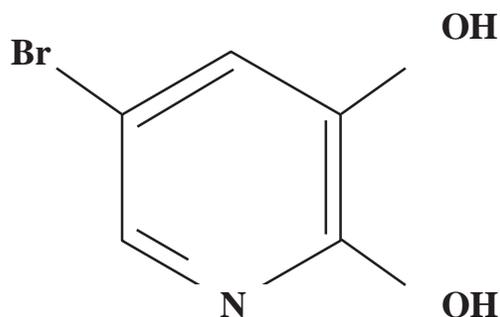
RESULT AND DISCUSSION

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

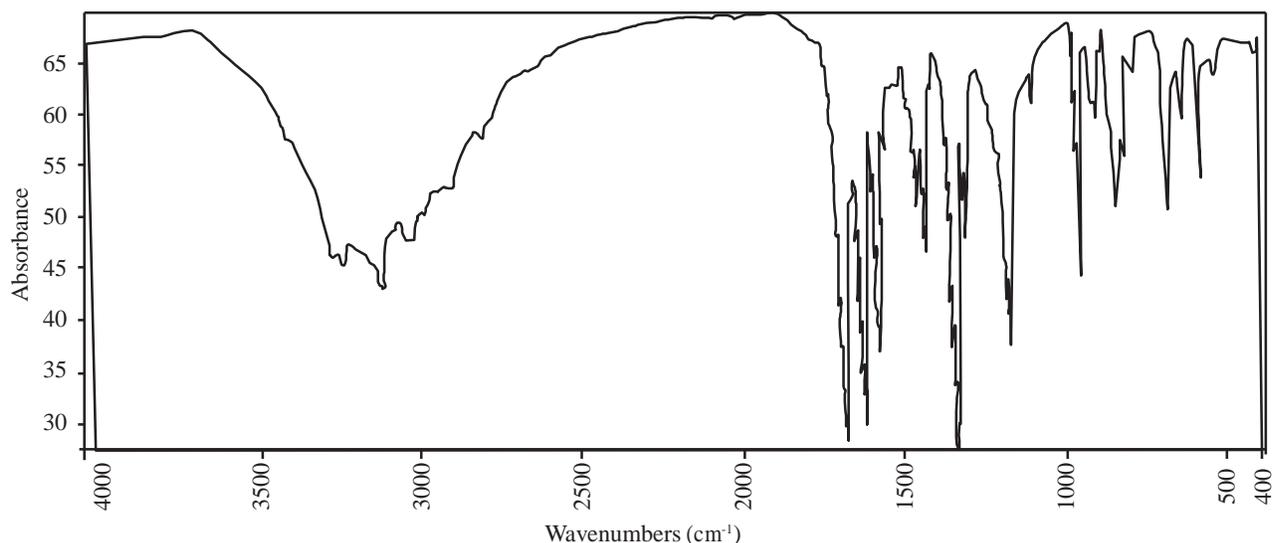
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Figure 1: Molecular structure of 5,2,3-BDHP

C-H Vibrations : Since the molecule 5,2,3-BDHP is a tri-substituted pyridine; therefore 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 lie in the region 3000-3100 cm^{-1} [10-12]. Two IR bands have been observed at 3105 cm^{-1} (KBr) and 3115 cm^{-1} (KBr) which have been assigned to this mode. These assignments are also in the agreement with the literature value [12-13]. Rao [14] has suggested that C-H in-plane and out-of-plane bending modes lie in the region 1000-1250 cm^{-1} and 700-900 cm^{-1} respectively. Gupta *et al.* [15] have assigned C-H in-plane bending mode at 1124 cm^{-1} in 4-hydroxy-3-methoxy benzaldehyde and out-of-plane bending mode at 790 and 828 cm^{-1} in 3-hydroxy-4-methoxy benzaldehyde while Goel and Atrey [16] have assigned C-H out-of-plane bending mode at 1245 cm^{-1} in 3-amino-2-chloro pyridine. Tripathi *et al.* [6] have assigned these modes in the region 1015-1180 cm^{-1} and 805-895 cm^{-1} in hydroxy pyridine.

Figure 2: IR Spectra of 5,2,3-BDHP in KBr pellets

In view of these assignments, the bands observed at 1110 cm^{-1} (KBr) and 1180 cm^{-1} (KBr) have been taken to represent in-plane bending modes 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 agreements with literature value [17-19].

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} [13,14,20,21]. 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 [13-14] (**Table 1**). The C-C-C trigonal bending vibrations have assignment with the literature value [13,14,22].

Due to the tautomeric behavior of the molecule, the N-H stretching frequency may appear in the molecule. Vir Singh

et al. [5] 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 stretching 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 [5,16]. Various other modes have also assigned in **Table 1** in their respective regions [14,23,24].

C-X Vibrations : Some researchers [25-26] have assigned (C-OH) Stretching mode around 1300 cm^{-1} in substituted benzene. *Gupta et al.* [15] have assigned this mode at 1262 , 12565 and 1270 cm^{-1} in hydroxy methoxy benzaldehyde while *Yadav et al.*[27] 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) has 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.

Sundaraganesan et al. [9] have assigned (C-Br) stretching mode at 527 cm^{-1} in 5-bromo-2-nitroPyridine. 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. As 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 of ring which shows the existence of C=O, N-H stretching and bending modes. *Vir Singh et al.*[5] 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 535 and 365 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 pellet techniques.

Group Vibrations (-OH groups) : In monomeric phenol [20, 28] the -OH stretching mode appears around 3600 cm^{-1} whereas in associated species it is reported in the region $3145\text{-}3430\text{ cm}^{-1}$ [15, 29]. *Goel et al.* [16] 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) has been taken to represent O-H stretching modes.

The spectra of substituted benzene shows, the O-H torsion mode as usually a weak band [14]. *Green et al.* [28] and *Siquenza et al.*[30] have assigned this mode near 420 cm^{-1} in penta chloro phenols, while *Faniran* [31] 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**

[13-14].

Table 1: Assignment of Vibrational Frequencies in (cm⁻¹) of 5,2,3-BDHP

IR	ASSIGNMENT
435 vw	(O-H) torsion, γ ring
527 w	β (C=O), γ ring, ν (C-Br)
570 ms	β (C-OH)
630 w	β ring
680 ms	β (C-OH)
785 w	ring breathing, C-N-C bending vibration
815 w	γ (C-H)
850 ms	trigonal bending
846 ms	(C-C-C) trigonal bending
trigonal bending	(C-C-C) trigonal bending
905 w	β (C-H)
960 ms (I)	β (C-H)
959 ms (I)	ν (C-OH)
(C-C-C) trigonal bending ν (C-Br)	ν (C-OH)
1110 w	ν ring
1180 s	ν ring
1177 s	ν ring
β (C-H)	ν ring
1310 ms	ν (C=O), β (N-H)
1345 s	ν (C-H)
1341 s	ν (C-H), ν (C-H)
ν (C-OH)	ν (O-H), ν_{sym} (N-H)
1430 ms	
1455 ms	
1575 s	
1615 s	
1611 s	
ν ring	
1680 s	
3105 vw	
3115 vw	
3240 w	
3270 vw	

Where : ν - stretching; vw- very weak
 β - in plane bending; w- weak
 γ - out-of-plane bending; ms - medium strong
 ν_{sym} - symmetric stretching s - strong.

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