

FTIR absorption spectra and thermodynamic functions of 5-chloro-2,3-dihydroxy pyridine

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Abstract : The infrared absorption spectra of 5-chloro-2,3-dihydroxy pyridine have been recorded in the region $400 - 4000 \text{ cm}^{-1}$. The bands observed in the IR spectra are discussed by assuming the compound under C_s point group symmetry. The modes of vibration for the different fundamentals have been proposed. The thermodynamic functions have also been calculated by using IR frequencies at different temperatures with the help of computer programming.

Keywords : Infrared and Raman spectroscopy, vibrational frequencies, thermodynamic functions.

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1. Introduction

The aromatic compounds like benzene, 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 acids [1-6]. The vibrational spectra of di-substituted pyridines have been studied by some worker [7,8], but very little work appears on the IR spectra of tri-substituted pyridines [9,10]. Further when the N-heterocyclic molecules have some substituent like -OH, -SH and -NH₂, they may cause tautomerism. In view of these, we discuss the vibrational spectra of 5-chloro-2,3-dihydroxy pyridine.

2. Experimental

Specpure grade chemical 5-chloro-2,3-dihydroxy pyridine was obtained from M/S Aldrich Chemie, West Germany and used as such. This chemical hereafter, referred as 5,2,3-CDHP. The purity of the said compound was also confirmed by elemental analysis and melting point determination. The infrared absorption spectra of 5,2,3-CDHP was recorded on Perkin Elmer spectrophotometer model-52 in the region $400-4000 \text{ cm}^{-1}$ using KBr pellet.

3. Results and discussion

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

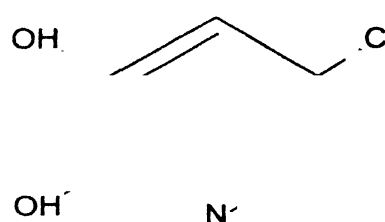


Figure 1. Molecular structure of 5-chloro-2,3-dihydroxy pyridine.

The IR spectra of 5,2,3-CDHP in KBr pellets is given in Figure 2. The fundamental vibrational frequencies of the said molecule are given in Table 1. The C_s point group symmetry has been assumed for the analysis of the said molecule. The thermodynamic parameters viz. free energy function $(F^\circ - E_0^0)/T$, entropy function S° , enthalpy function $(H^\circ - E_0^0)/T$, and heat capacity function C_p^0 with absolute temperature are given in Table 2 for 5,2,3-CDHP. The variation of free energy and entropy function

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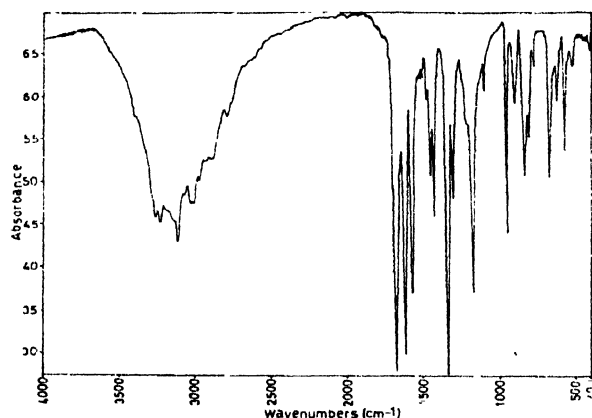


Figure 2. IR spectrum of 5,2,3-CDHP in KBr pellet

Table 1. Assignment of vibrational frequencies in (cm^{-1}) of 5,2,3-CDHP.

IR	Assignment
431 vw	(O-H) torsion, γ ring
520 w	β (C=O), γ ring
565 ms	β (C-OH)
626 w	β ring
676 ms	β (C-OH)
782 w	ring breathing, C-N-C bending vibration
814 w	γ (C-H)
846 ms	trigonal bending
904 w	(C-C-C) trigonal bending
959 ms	(C-C-C) trigonal bending, ν (C-Cl)
1106 w	β (C-H)
1177 s	β (C-H)
1309 ms	ν (C-OH)
1341 s	ν (C-OH)
1427 ms	ν ring
1450 ms	ν ring
1571 s	ν ring
1611 s	ν ring
1677 s	ν (C=O), β (N-H)
3103 vw	ν (C-H)
3111 vv	ν (O-H), ν (C-H)
3237 w	ν (O-H)
3266 vw	ν_{sym} (N-H)

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.

with temperature is shown in Figure 3, while that of enthalpy and heat capacity function with absolute temperature is shown in Figure 4 for 5,2,3-CDHP.

Table 2. Thermodynamic functions of 5,2,3-CDHP (Cal./Mole-K).

Temperature (K)	$-(F^\circ - E_0^0)/T$	S°	$-(H^\circ - E_0^0)/T$	C_p^0
200	59.29	21.47	12.78	21.47
300	65.28	29.12	16.99	29.12
400	70.71	35.66	20.80	35.66
500	75.75	41.20	24.40	41.20
600	80.48	45.79	27.59	45.79
700	84.96	49.59	30.47	49.59
800	89.20	52.75	33.06	52.75
900	93.23	55.39	35.40	55.39
1000	97.07	57.61	37.51	57.61
1100	100.74	59.49	39.43	59.49
1200	104.25	61.08	41.17	61.08
1300	107.61	62.44	42.75	62.44
1400	110.83	63.61	44.20	63.61
1500	113.93	64.61	45.53	64.61

S° = entropy, F° = free energy, E_0^0 = zero point energy, $(H^\circ - E_0^0)$ = enthalpy, C_p^0 - heat capacity.

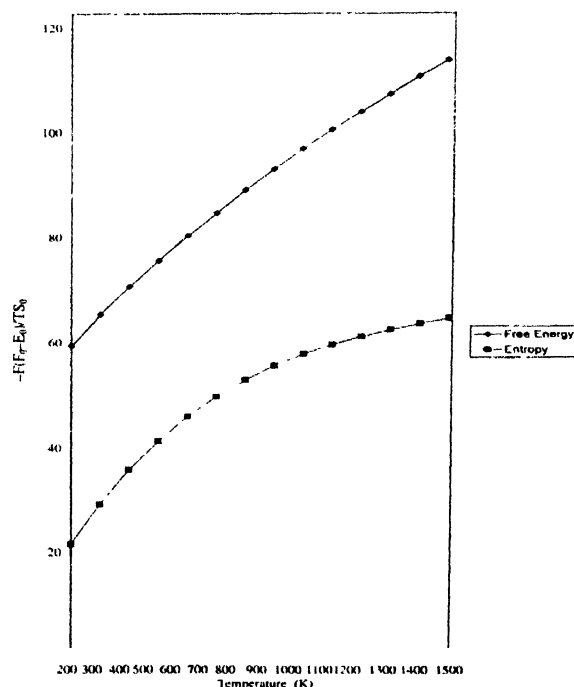


Figure 3. Temperature vs. free energy and entropy for 5,2,3-CDHP.

3.1. Vibrational spectra :

3.1.1. Ring vibrations :

3.1.1.1. C-H Vibrations :

Since the molecule 5,2,3-CDHP is a tri-substituted

pyridines, it has two hydrogen atoms left around the ring. Thus, the compound 5,2,3-CDHP may have two C-H valence oscillations which usually lie in the region $3000 - 3100\text{cm}^{-1}$ [11]. Two IR bands have been observed at 3103cm^{-1} and 3111cm^{-1} which have been assigned to this mode. These assignments are also in agreement with the literature value [12]. Rao [13] has suggested that C-H in-plane and out-of-plane bending modes lie in the region $1000 - 1250\text{cm}^{-1}$ and $700 - 900\text{cm}^{-1}$, respectively. Gupta *et al* [14] have assigned C-H in-plane bending mode at 1124cm^{-1} in 4-hydroxy-3-methoxy benzaldehyde and out-of-plane bending modes at 790 and 828cm^{-1} in 3-hydroxy-4-methoxy benzaldehyde while Goel and Atrey [15] have assigned C-H out-of-plane bending mode at 1245cm^{-1} in 3-amino-2-chloro pyridine. Tripathi and Pandey [9] have assigned these modes in the region $1015 - 1180\text{cm}^{-1}$ and $805 - 895\text{cm}^{-1}$ in hydroxy pyridine.

In view of these assignments, the bands observed at 1106cm^{-1} and 1177cm^{-1} have been taken to represent in-plane bending modes while the bands observed at 814cm^{-1} and 846cm^{-1} have been taken to represent C-H out-of-plane bending modes. These assignments are also in agreement with the literature values [16,17].

3.1.1.2. 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 $690-844\text{cm}^{-1}$ [12,13]. The IR band observed at 782cm^{-1} 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 [12,13] (Table1). The C-C-C trigonal bending vibrations have been assigned at 904cm^{-1} and 959cm^{-1} while C-N-C trigonal bending vibration has been assign at 782cm^{-1} which are in agreement with the literature values [12,13,18].

Due to the tautomeric behaviour of the molecule, the N-H stretching frequency may appear in the molecule. Vir Singh *et al* [5] have assigned this mode at 3230cm^{-1} in 2,4-dihydroxy-6-methyl pyrimidine. In view of this assignment, a weak IR band observed at 3266cm^{-1} has been assigned to N-H stretching mode of vibration while the band observed at 1677cm^{-1} has been assigned to N-H in-plane bending mode of vibration. This also finds support from the literature [8,15]. Various other modes have also been assigned in Table .1 in their respective regions [13,19].

3.1.1.3. C-X vibrations :

Some workers [20,21] have assigned (C-OH) stretching mode around 1300cm^{-1} in substituted benzene. Gupta *et al* [14] have assigned this mode at 1262 , 1265 and 1270cm^{-1} in hydroxy methoxy benzaldehyde, while Yadav *et al* [22] have assigned this mode at 1270cm^{-1} in the identical compound.

In view of these assignments, the bands observed at 1309cm^{-1} and 1341cm^{-1} have been assigned to this mode. The (C-OH) in-plane bending modes have been assigned at 565cm^{-1} and 676cm^{-1} in the compound 5,2,3-CDHP.

Goel and Agarwal [23] have assigned (C-Cl) stretching mode at 1065 and 1055cm^{-1} in 3-amino-2-chloro pyridine and in 5-chloro-2,4-dimethoxy aniline. In view of these assignments, the band observed at 959cm^{-1} (KBr) has been taken to represent (C-Cl) stretching mode in 5,2,3-CDHP. 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* [8] have assigned a medium strong band at 1700cm^{-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 360cm^{-1} in the same molecule. In view of this, the strong IR band at 1677cm^{-1} has been assigned as (C=O) stretching mode of vibrations, while the IR band observed at 565cm^{-1} has been assigned as (C=O) in-plane bending mode of vibration. Both the bands are taken in KBr pellet techniques.

3.1.2. Group vibrations :

3.1.2.1. -OH group :

In monomeric phenols [24], the -OH stretching mode appears around 3600cm^{-1} whereas in associated species [14,25], it is reported in the region $3145-3430\text{cm}^{-1}$. Goel *et al* [28] have assigned this mode at 3560cm^{-1} in 4,6-dihydroxy-2-mercapto pyrimidine. In view of these, the bands observed at 3111cm^{-1} (KBr) and 3237cm^{-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 [13]. Goel and Agarwal [23] and Siquenza *et al* [26] have assigned this mode near 420cm^{-1} in penta-chloro-phenols, while Faniran [27] have assigned this mode at 314 and 318cm^{-1} in

penta-bromo and penta-chloro-phenols. During the presents investigation, these modes have been identified at 431 cm^{-1} . The various other modes of this group have been assigned in their own regions in the Table 1.

4. Thermodynamic functions

The thermodynamic parameters viz. heat capacity C_p^0 , enthalpy $(H^0 - E_0^0)/T$ and entropy function S^0 of the compounds 5,2,3-CDHP have been computed by using the standard expressions [28,29] by taking X-axis to pass through the para position and Y-axis perpendicular to molecular plane. For determining the rotational contribution, the structural parameters give in Table 3 were used [30,31].

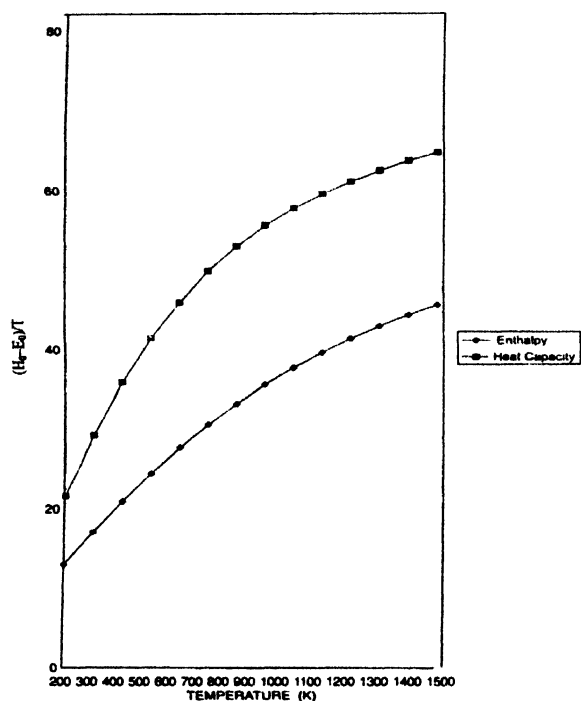


Figure 4. Temperature vs. free energee and heat capacity for 5,2,3-CDHP.

The thermodynamic functions have been calculated at different temperature between 200–1500 K by using (3n-6) fundamental frequencies for the said compound and assuming rigid rotator harmonic oscillator approximation. The calculations were performed for one mole of an ideal gas at one atmospheric pressure. The symmetry number for overall rotation and internal rotation has been taken as two. The principle moment of inertia were found to be 0.3863, 0.8615 and $1.2478 \times 10^{-37} \text{ gm cm}^2$ for the said molecule. All the thermodynamic parameters

are plotted as function of temperature (Figures 3,4). From graphs, it was found that all the thermodynamic parameters rise more rapidly in the low temperature range and less rapidly in the high temperature range.

Table 3. Structural parameters.

Bond length (Å)	Bond angles (°)
$N_1C_2 = 1.43$	$\angle N_1C_2C_3 = 120^\circ$
$C_2C_1 = 1.33$	$\angle C_2C_3C_4 = 120^\circ$
$C_1C_4 = 1.32$	$\angle C_3C_4C_5 = 120^\circ$
$C_4C_5 = 1.39$	$\angle C_4C_5C_6 = 120^\circ$
$C_5C_6 = 1.39$	$\angle C_5C_6N_1 = 120^\circ$
$C_6N_1 = 1.38$	$\angle C_6N_1C_2 = 120^\circ$
$C_2O_7 = 1.35$	$\angle N_1C_2O_7 = 121^\circ$
$C_1O_8 = 1.43$	$\angle C_3C_2O_7 = 119^\circ$
$C_3C_{10} = 1.75$	$\angle C_2C_1O_8 = 122^\circ$
	$\angle C_4C_3O_8 = 118^\circ$
	$\angle C_4C_5C_{10} = 118^\circ$
	$\angle C_6C_5C_{10} = 122^\circ$

At very high temperature greater than 1500 K, the influence of anharmonicity will be large and the expressions used for the calculation will not give an accurate value of thermodynamic parameters. The trend of variations of thermodynamic parameters is similar to those reported for the similar molecules in the literature [32–35].

This study has become more relevant in view of its great biological importance and the thermodynamics will used as an important tool, in the field of research.

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