Study of Infrared Spectrum And Thermodynamic Functions of 4-Amino-2,6- Dihydroxy Pyrimidine

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Abstract

The present study investigates the infrared spectra of 4-amino-2,6-dihydroxy pyrimidine in the range of $400 - 4000$ cm^{-1}. The proposed assignment is based on the group frequency approach together with the data available for molecule similar in nature. The thermodynamic functions have also been computed and discussed.

Keywords: 4,2,6,ADHP; thermodynamic functions; frequency approach; uracils; thymines

INTRODUCTION

The pyrimidine when substituted with OH, CH_3 and NH_2 gives us biologically important molecules like cytosine, thymine and uracils etc. Due to significant role of N-hetrocyclics into the structural problems of nucleic acids, investigations on substituted pyrimidines draw considerable attention. In such type of molecules the role of substituent is very important. Even so, few detailed spectroscopic studies have been reported in literature for pyrimidine[1-4], substituted pyrimidine [5-11] and that nucleic acid constituents[12-15]. Because of low symmetry and limited information about the molecular parameters, reliable theoretical calculations for such molecules are not possible. Thus it was considered to understand the role of substituents by experimental method. It has been possible to have tautomeric structures with substituent like OH and NH_2 as reported in case of 4-5-diamino pyrimidine and 4-6-dihydorxy pyrimidine by Srivastava et-al[16]. In the present investigations the role of

the NH_2 group by changing its position around the ring in the presence of two OH groups by spectroscopic methods are discussed. For this study the infrared spectra of molecule 4-amino-2,6-dihydroxy pyrimidine was recorded and tautomeric behaviour in this molecule structure is discussed with vibrations associated with NH_2 and OH groups.

EXPERIMENT

The infrared spectra of 4-amino-2,6-dihydroxy pyrimidine (hereafter called 4,2,6-ADHP) has been recorded by nujol mull techniques. The accuracy of the bands is up to ± 10 cm^{-1} in the 400-2000 cm^{-1} and ± 20 cm^{-1} in the region 2000-4000 cm^{-1}.

RESULTS AND DISCUSSION

In view of the position of the substituent the molecule 4,2,6-ADHP falls under C_5 point group symmetry as shown in Fig.I.
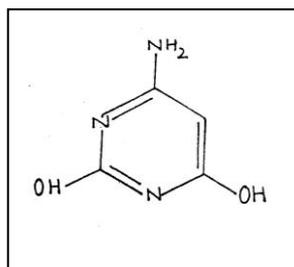

Figure –I: 4-Amino-2,6- Di-Hydroxy Pyrimidine

In this discussion only important ring vibrations are chosen as substituent does not exert much influence on the vibrations associated with C-H bond and other functional groups listed in table I. In infrared spectra of pyrimidine, two pairs of absorption bands at 1400, 1461 cm^{-1} and 1569, 1610 cm^{-1} have been observed which arise due to interaction effects of the ring double bonds. By this argument the two pairs of bands at 1400, 1480 cm^{-1} and 1534, 1620 cm^{-1} in 4,2,6-ADHP molecule have been assigned to the ring stretching vibrations. The spectral studies of pyrimidine and substituted pyrimidine[17,18] shows that breathing vibration corresponding to ν_1 mode of benzene is mass depending accordance to that which is proposed by Lord et-al[1]. By observed bands together with the data available for tri-substituted benzenes the ν_1 mode has been assigned at 780 cm^{-1} in the present molecule. The ν_{12} and ν_{14} modes are not sensitive to the mass substituent, so these are assigned at 1020 and 1400 cm^{-1} in 4, 2, 6-ADHP Molecule. Mode ν_6 is mass sensitive and are found in substituted

aromatic molecules and tri-substituted benzenes the pair of bands at 526 and 552 cm^{-1} in 4, 2, 6- ADHP molecule has been assigned as part of above mode. Sullivan and Sadler[19] have suggested occurrence of bands between 3120-2900 cm^{-1} in indole-3-aldehyde corresponding to N-H stretching frequencies due to strong intra-molecular hydrogen bonding, according to Szczezesnaik et-al[20], bands observed in the infrared spectra of 1-methyl uracil in the region 3100-2800 cm^{-1} are due to hydrogen bonded N-H stretching frequencies. Rao[21] has suggested that N-H stretching frequencies in the range 3300-3150 cm^{-1} are due to intermolecular association through NH=O hydrogen bonding. The existence of C=O stretching shows the migration of H atom from OH group at position 2 to the N atom of the ring in given molecule at the same time the presence of a weak OH stretching mode similarly indicates that migration of H atom of OH is not complete. The presence of weak OH stretching further suggests that the OH group is involved in hydrogen bonding. The hydrogen bonding which stabilizes the ground state will be weakened by the shift of electron density away from the non-bonding centre upon excitation and a blue shift of band will be observed relative to the band position in a non-hydrogen bonding solvent. The unbounded or free hydroxyl group absorbs strongly in the region 3650 -3580 cm^{-1}. But intra-molecular or inter-molecular bonding usually, shifts the absorption to lower frequencies. A broad extended band is characteristic of intra-molecular bonding whereas splitted bond suggests inter-molecular bonding. The same is not present in this molecule, hence there is no hydrogen bonding in present case. The tautomerism is shown in fig. II.

Table – I: Infrared assignments of 4-Amino-2,6- Di-Hydroxy Pyrimidine

I.R. Bands	Intensity	Assignments
430	w	Ring o. p.b.
465	w	Ring o.p.b
526	vs	Ring o.p.b
552	s	(C-OH) i.p.b.
625	s	NH2 Wagging
665	w	(C-OH) i.p.b.
690	w	Ring i.p.b.
710	w	(C-H) o.p.b.
780	s	Ring breathing
995	w	(C-H) i.p.b.
1020	m	Ring i.p.b.
1060	n	(C-NH2) i.p.b.

I.R. Bands	Intensity	Assignments
1250	m	(C-OH) stretching
1295	m	(C-OH) stretching
1400	vs	(C-NH2) stretching (Ring stretching)
1480	ms	Ring stretching
1534	M	Ring Stretching
1620	b	Ring stretching
3020	m	(C-H) stretching
3300	w	(N-H) symmetric stretching
3400	s	(N-H) asymmetric stretching

vs = very strong. i.p.b. = in- plane bending, s = strong,

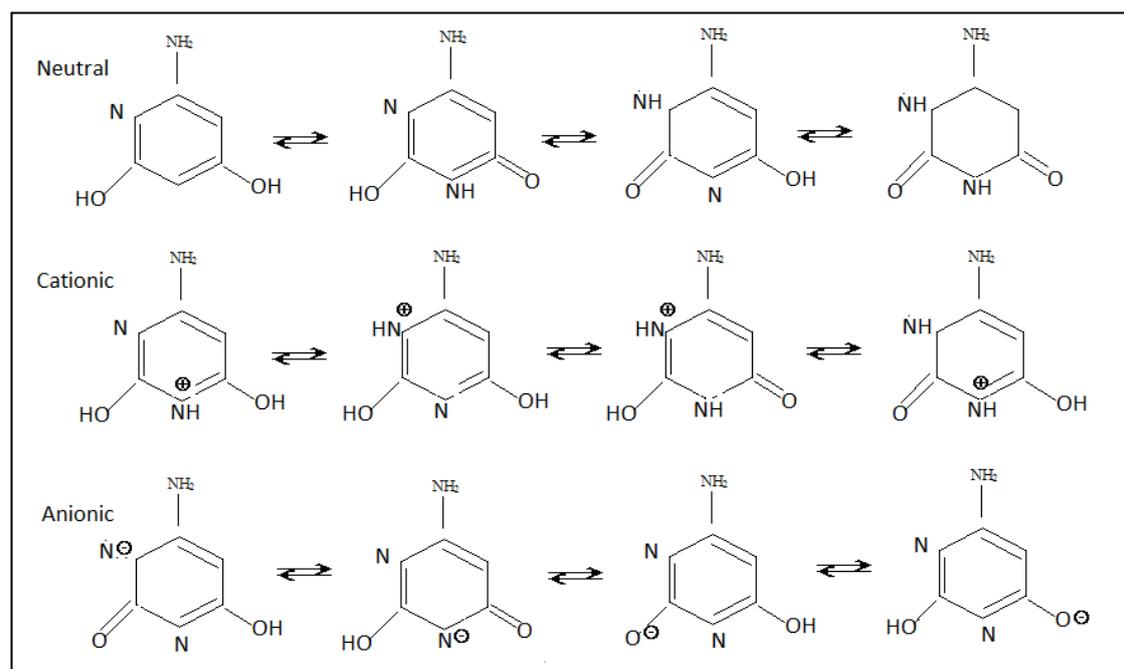o.p.b. = out of plane bending, m = medium, w= weak, b = broad.

Figure –II: Tautomeric Form of 4-Amino-2,6- Di-Hydroxy Pyrimidine

C-H stretching mode exists between 3000 - 3100 cm^{-1} [22]. In view of it, the band at 3020 cm^{-1} with medium intensity has been assigned to C-H stretching mode in the title molecule 4,2,6-ADHP. According to Kletz and price[23], C-OH stretching frequency occurs around 1300 cm^{-1} in substituted phenol. In view of above the observed band at 1250 and 1295 cm^{-1} have been assigned as C-OH stretching mode in

the present study, since OH group substitution at 2 and 6 positions., Many workers[24] have found that C-NH$_2$ stretching vibration appears near 1350 cm$_{-1}$. However, in some spectra it may have been some contribution from C-C stretching of benzene. In the present study the strong band observed at 1400 cm^{-1} has been correlated to C-NH$_2$ stretching band. Bellamy and Williams[25] have shown that symmetric and asymmetric N-H stretching vibrations obey the empirical relation.

$$\nu_{sym} = 345.53 + 0.876 \, \nu_{asym} \tag{1}$$

Under the present investigation the bands at 3300 and 3400 cm^{-1} have been correlated to symmetric and asymmetric stretching vibrations. Bellamy[25] suggested that in N-Octamide the NH$_2$ free absorption occurs at 3530 and 3415 cm^{-1} in chloroform solution and it also shown the additional bands at 3490, 3345, 3300 and 3182 cm^{-1}. This indicates the occurrence of different types of simultaneous association of free and bonded N-H bands. It supports the above assigned N-H stretching bands of the present molecule. Goel et-al[10] have assigned in- plane and out-of plane bending vibrations respectively. In the present study the C-NH$_2$ in- plane bending vibration has been shown at 1060 cm^{-1}. The O-H valence vibration appears in the region 3500-3700 cm^{-1} in molecules having OH group. But such vibrations could not appear in the present study.

THERMODYNAMIC FUNCTIONS:

Thermodynamic functions viz enthalpy (H$_o$ –E$_{oo}$) /T, heat capacity C$_{op}$, free energy (F$_o$– E$_{oo}$) /T, and entropy So of the title compound 4,2,6- ADHP have been computed using the standard expression[26,27], by taking Y axis perpendicular to the molecular plane and Z axis to pass through the para positions. For determining rotational contribution the following structural parameters were used[28-29].

N$_1$-C$_2$ = 1.32Å	∠ N$_2$C$_4$N$_3$ = 121°
C$_2$ –N$_2$ = 1.28 Å	∠ C$_5$C$_4$N$_3$ = 119°
N$_2$-C$_4$ = 1.39 Å`	∠ C$_5$C$_6$O$_1$ = 122°
C$_4$-C$_5$ = 1.29 Å	∠ N$_1$C$_6$O$_1$ = 121°
C$_5$ – C$_6$ = 1.38 Å	∠ N$_1$C$_2$O$_2$ = 123°
C$_6$ – N$_1$ = 1.27 Å	∠ N$_2$C$_2$O$_2$ = 118°
C$_6$ –O$_1$ = 1.27 Å	∠ C$_6$N$_1$C$_2$ = 118°
C$_2$ - O$_2$ = 1.31 Å	∠ C$_2$N$_2$C$_4$ = 123°
C$_4$-N$_3$ = 1.29 Å	All other angles were taken as 120° in the ring.

Thermodynamic functions have been calculated at different temperatures between 100-1500°K using fundamental frequencies and assuming rigid rotor harmonic oscillator approximation. The calculations were performed for one mole of an ideal gas at 1 atmospheric pressure. The symmetry number for overall rotation has been taken as 2 and internal rotation as 2. The principal moments of inertia were found to be 45.70 76.36 and 30.66 gm x cm^2 in this molecule. While reduced moment of inertia is 9.88 gm x cm^2. The variation of potential barrier and thermal energy with absolute temperatures have been reported in table II for molecule 4,2,6-ADHP and shown graphically in fig III, which are in agreement with the trend reported in literature.

Table –II: Potential barrier and Thermal Energy of 4-Amino-2,6- Di-Hydroxy pyrimidine.

Temperature Deg. Kelvin	Potential Barrier	Thermal Energy
100	0.0120	22.77
200	0.0060	16.10
273	0.0043	13.78
298	0.0040	13.20
300	0.0039	13.15
400	0.0029	11.38
500	0.0024	10.18
600	0.0020	9.30
700	0.0017	8.60
800	0.0015	8.04
900	0.0013	7.59
1000	0.0012	7.00
1100	0.0011	6.86
1200	0.0010	6.57
1300	0.0009	6.31
1400	0.0008	6.08
1500	0.0007	5.88
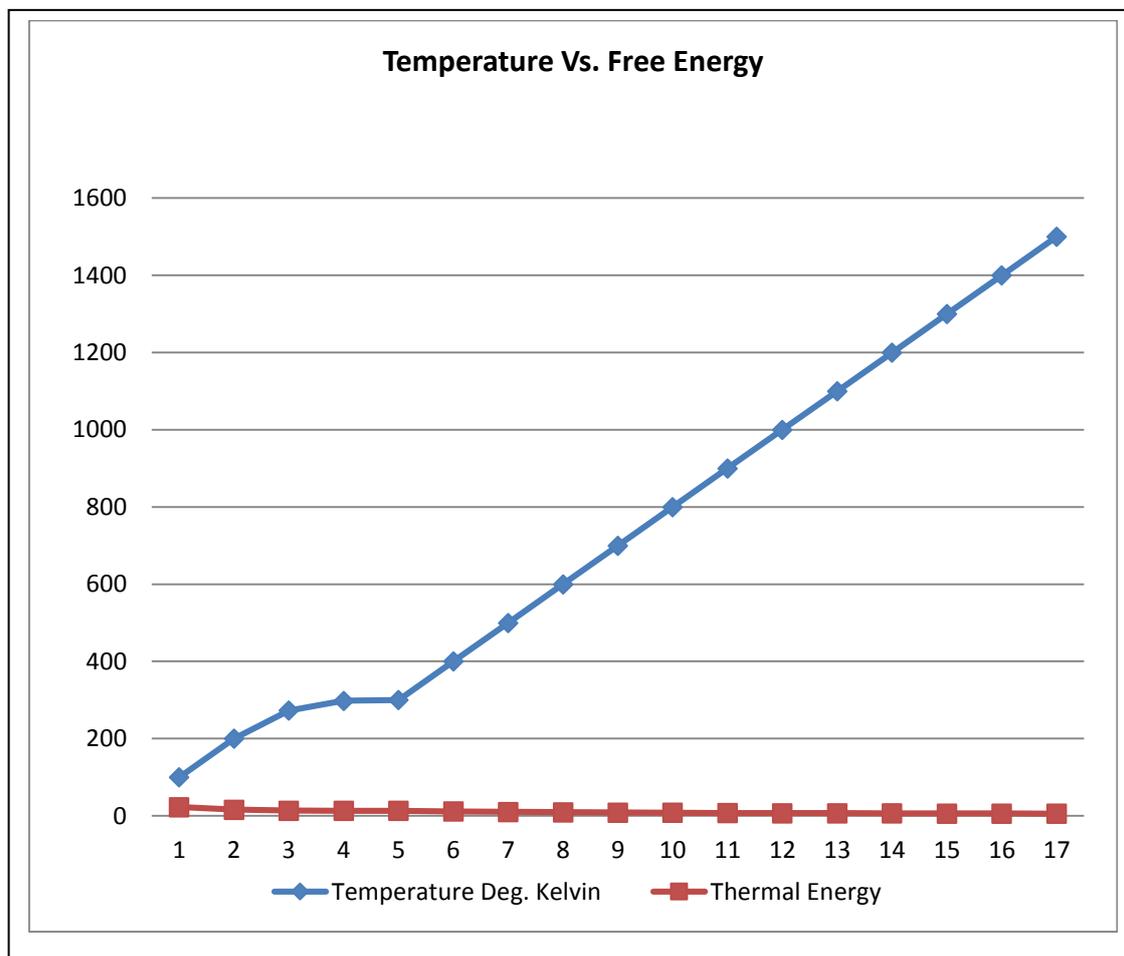
Figure –III: Temperature Vs free energy

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