Vapour Phase Ultraviolet Spectrum Of Amino Hydroxy Pyrimidine

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Abstract: This paper comprises of the investigations on the electronic spectra in vapour phase of the experimental molecule 2,5-diamino-4,6-dihydroxy pyrimidine has been recorded in the region 2000 – 3600 Å. The two electronic band system due to n–π* and π-π* transitions have been observed corresponding to 2100 Å and 3000 Å systems of pyrimidine respectively. The ultraviolet assignments have been discussed in terms of ground and excited state fundamental mode and their combinations.

Introduction: Amongst in the N-heterocyclic molecules, the pyrimidine when substituted with hydroxy (OH), methyl (CH_3) and amine (NH_2) gives us biological important molecule like cytosine, thymine and uracil etc. The investigations of substituted pyrimidine draw considerable attention because of significant role of N-heterocyclic molecule into the structural problems of nucleic acid. In these molecules, the role of substituent plays a very significant role. As on dated, some detailed spectroscopic studies have been reported in the literature value for pyrimidine and substituted pyrimidine [1,2] and nuclei acid constituent [3,4]. The absorption spectra of uracil and cytosine nucleosides have been well predicted on theoretical ground by Berthod et al [5]. Some workers [6,7] have found evidence of the presence of electronic transition other than n-π* and π-π* in the spectra of cytosine as well as in uracil with their nucleosides also.
Therefore, the detailed study of the electronic transitions of the substituted pyrimidine is of good importance to find the presence of n-π*, π-π* and n-σ* transitions. A good number of researchers [8,9] have studied the electronic absorption spectra of substituted pyrimidines. The ultraviolet (electronic) absorption spectra of pyrimidine have been studied by Uber [10] and Innes et al [11]. They observed that it shows a strong absorption system near 3200 Å. The band at 2430 Å system is analogous to the 2600 Å system of benzene and does not indicate any vibrational spectra while the band at 3200 Å shows a large number of discrete bands and vibrational analysis has bee suggested for the same [10].

Innes et al [11] studies the rotational analysis which reveals that this system appears because of $\tilde{A}^1B_1$ – $\check{Z}^1A_1$ transitions. Shashidhar et al [12] also studied the 2400 Å system in methyl pyrimidines. Many workers [11] have been studied the electronic states of azobenzene in detail both theoretically as well as experimentally. The study of substituted azobenzene would be of great importance in explaining some ambiguities regarding the vibrational assignments and geometrical structure of parent molecule. Moreover, these types of molecules are of great biological importance. In view of this, the present article reports the study of Vapor phase near ultraviolet spectra and spectral analysis of vapor phase ultraviolet spectra in terms of ground as well as in the excited state 2,5-diamino-4,6-dihydroxy pyrimidine.

Experimental Details :

Spectroscopic grade sample of 2,5-diamino-4,6-dihydroxy pyrimidine (hereafter referred as 2,5,4,6-DADHP) have been taken. The vapor phase ultraviolet spectra of present molecule was recorded on Beckman DK-2A ratio recording spectrophotometer using cell of 10 cm^{-1} path maintained at different temperatures from 30ºC to 70ºC. The techniques for the analysis of spectra find support from the literature value [3,4].

Result and Discussion:

The molecular structural formula of the compound 2,5,4,6-DADHP is shown in Figure 1.

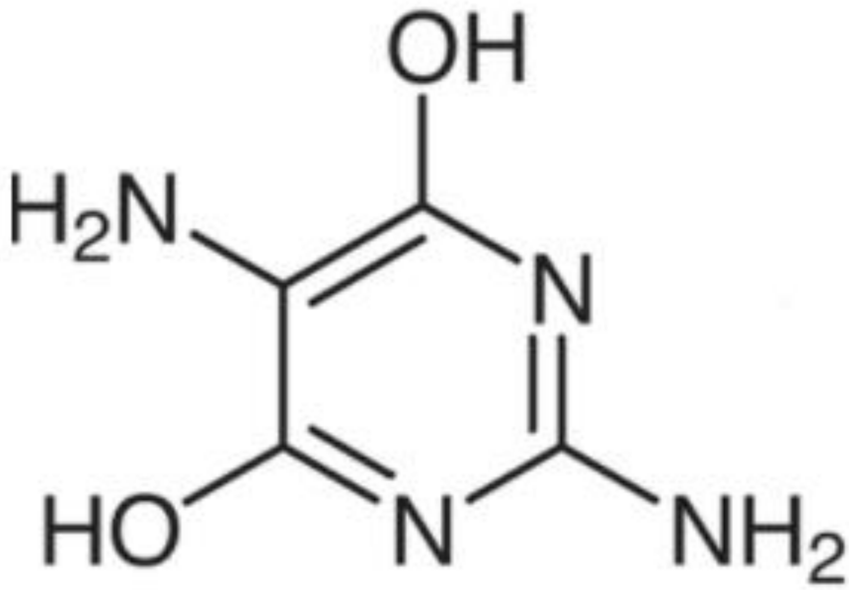

FIGURE: 1 MOLECULAR STRUCTURE OF 2,5,4,6-DADHP

Methyl group frequencies with their correlation to other molecules, analysis of electronic bands with excited state and ground state fundamentals, a correlation of n-π* and π- π* transitions with the similar molecules are shown in Table – 1 to 3 respectively.

Electronic Spectra:

The wave number of vibronic bands, both ground state and excited state fundamentals, with their approximate intensities and probable assignments for the said molecule as given in Table 1 with complete analysis with overtones and combination of bands. For correlation, the observed electronic ground and excited state fundamentals with their approximate intensities and probable assignments for the title molecule with complete analysis with overtones and combination of bands. For correlation, the observed electronic ground and excited state fundamental frequencies together with reported infrared and laser Raman frequencies are shown in Table-1. The 0,0 band of both systems are compared at the bands of other molecules are given in Table-2. The observed spectra shows two band systems lying in the region 3100-2100 Å. As discussed earlier, the system close to higher wavelength has been correlated with the n-π* system and that near to lower wavelength, which is very strong as expected to the π-π* system of the pyrimidine. These assignments find support from the literature value [2,9] and a red shift has been reported for the same [10]. However, in the said molecule 2,5,4,6-DADHP, the shift is undoubtedly blue that has been verified through different records in vapor phase at different temperatures. The strong band towards the higher wavelength side at 45558 cm^{-1} has been identified as the 0,0 band of the π-π* system.

A large number of bands appear towards the shorter wavelength side of the 0,0 band. The strongest band towards the higher wavelength side at 33780 cm^{-1} has been identified as the 0,0 band of the n-π* system in the present study. It also indicates a blue shift compared to dichloride pyrimidines [12] and methyl pyrimidines [10,12].

In conformity to the permitted nature of the transition and nature of the observed absorption spectrum in vapor phase recorded at different wavelength of the absorbing path and different temperatures, the molecule 2,5,4,6-DADHP have two distinct fairly intense systems (system I & II) of bands. On the basis of the similar assignments in case of substituted pyrimidines [8,12], the first band system begin from about 33780 cm^{-1} is assigned as n-π* transition and the second system of band that extends from 47619 cm^{-1} towards the higher wavelength side is assigned to π-π* transition. It has been observed from the Table–1 that the band system lying on a shorter wavelength side consists of well resolved bands. The very short band observed at 33780 cm^{-1} is assigned as 0,0 band. It find support from the literature value [3,4]. On the shorter wavelength side of 0,0 band, we found some good bands which are separated from it by 57, 113, 170, 226, 283, 339, 450, 533, 561, 616 cm^{-1} are assigned to excited state fundamentals. On the other side of 0,0 band with spacing 57, 172, 230, 288, 346, 405, 463, 522, 581 cm^{-1} are assigned to ground state fundamentals. All the infrared and laser Raman frequencies show a very correlation between ground state and excited state frequencies assigned to C-Cl in-plane and out-of-plane bending.

The ground state fundamentals with excited state value are well correlated with the vibrational values and are assigned to C-C stretching in-plane and out-of-plane bending. On the other hand, as seen from the Table–1 and 2, another strong system of band is observed in which the strong band at 47619 cm^{-1} is assigned to 0,0 band of the system of π-π* transition. The ground state and excited state fundamentals are well shown in Table-1 and 2. The band reported by 226, 450, 671, 891, 1108, 1323 cm^{-1} are assigned to ground state fundamentals. The bands have spaced at 227, 457, 690, 924, 1161 cm^{-1} are assigned to excited state fundamentals.

The n-π and π-π* transitions are identified for the present molecule 2,5,4,6-DADHP. These assignments show a very good correlation with the similar molecules which are given in Table 3. All these assignments are in good agreement with the literature values [13-15].

Table – 1

Analysis of Electronic Bands of 2,5-diamino-4,6-dihydroxy pyrimidine (All values are in cm^{-1})

Wave no & relative intensity	Separation from 0,0 band (n-π*) system I
33164	0 – 616
33219	0 – 561
33274	0 – 533
33330	0 – 450
33441	0 – 339
33497	0 – 283
33554	0 – 226
33610	0 – 170
33667	0 – 113
33723	0 – 57
33780 vvs	0 0 band
33837	0 + 57
33895	0 + 115
33852	0 + 172
34010	0 + 230
34068	0 + 288
34126	0 + 346
34185	0 + 405
34243	0 + 463
34302	0 + 522
34361	0 + 581

Table – 2

Analysis of Electronic Bands of 2,5-diamino-4,6-dihydroxy pyrimidine (All values are in cm^{-1})

Wave no & relative intensity	Separation from 0,0 band (n-π*) system II
46296	0 – 1323
46511	0 – 1108
46728	0 – 891
46948	0 – 671
47169	0 – 450
47393	0 – 226
47619 vvs	0 0 band
47846	0 + 227
48076	0 + 457
48309	0 + 690
48543	0 + 924
48780	0 + 1161

Table 3
Correlation of n-π* & π-π* transitions of 2,5,4,6-DADHP with identical molecules (All values are in cm^{-1})

Molecules	n-π* transitions	π-π* transitions
2,4,6-TAP	38000	42000
4,5-DAP	-	44000
2,4-AMP	36101	43937
2,4,6-ACMP	33670	42372
2,4,6-ADCP	33783	45558
2,5,4,6-DADHP	33782	47621

Where 2,4,6-TAP = 2,4,6-triamnino pyrimidine
4,5-DAP = 4,5-diamino pyrimidine
2,4-AMP = 2-amino-4-methyl pyrimidine
2,4,6-ACMP = 2-amino-4-chloro-6-methyl pyrimidine
2,4,6-ADCP = 2-amino-4,6-dichloro pyrimidine
2,5,4,6-DADHP = 2,5-diamino-4,6-dihydroxy pyrimidine

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