

VAPOUR PHASE U.V SPECTRA OF 5-BROMO-2, 4(1H, 3H)-PYRIMIDINEDIONE**Dr Sushil Kumar**Assistant Professor
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ABSTRACT: The vapor phase electronic spectrum of 5-Bromo-2,4(1H,3H)-pyrimidinedione have been recorded in the region 200-360 nm and interpreted according to the 3200 Å & 3930 Å systems of pyrimidine, in terms of ground & excited state fundamental modes and combinations for present molecules and depicted by assuming C_s point group symmetry. The analysis of electronic modes in terms of ground and excited state modes with $\pi-\pi^*$ & $n-\pi^*$ transitions having two band systems are depicted.

KEYWORDS: electronic transitions, Vapor phase, UV spectra.

INTRODUCTION

The aromatic compounds like benzene & their derivatives are having a valuable place in biophysics, biochemistry & pharma sector. The entire medicine, chemical, biological industries depend on these. [1-3]

N-heterocyclic compounds such as Adenine, Guanine, Cytosine, Thymine, Uracil, Pyridine, Purine etc are of great importance in all aromatics because of great biological interest as they are basic constituents of DNA & RNA. In addition DNA normally contains uncommon nucleotides usually in very small amount. In these N-heterocyclics, Pyrimidine and their derivatives are of notable antifungal, antibacterial, biological & pharmaceutical importance [4,5] various spectroscopic studies of these compounds have been traced out & motivated in analyzing the complex system [6,7]. The analysis of dizziness of N-heterocyclic may provide some evidence about outstanding structural problems due to low symmetry & limited information. Reliable theoretical calculations for such molecules are not possible. Thus it was considered to understand the role of constituents by experimental methods. The first publications of spectra of pyrimidines are due to Blout and Fields [8,9]. Randals et al. [10]. Not only this several research workers such as Susi & Ard [11], Najad & Stidham [12] have studied the I.R. & Raman spectrum of pyrimidine & its derivatives with experimental & theoretical calculations.

The absorption spectra of pyrimidine with uracil & cytosine nucleosides have been well predicted theoretically by Berthod et. al. [13]. Nesbet [14] Experimentally, Miles et. al. [15] have found evidence of the presence of electronic transitions other than $n-\pi^*$ and $\pi-\pi^*$ in the spectra of pyrimidine, uracil and cytosine and their nucleosides.

Thus the detailed study of the electronic transitions of the substituted pyrimidine is of great importance in order to check the presence of $n-\pi^*$ and $\pi-\pi^*$ and $n-\sigma$ transitions. Several workers [16] have studied the electronic absorption spectrum of substituted pyrimidines.

The electronic absorption spectrum of pyrimidine has been studied in detail by Uber [17] & Innes et al. [18] Who found that it presents a strong absorption system around 3200 Å. The 2430 Å system is analogous to the 2600 Å system of benzene and does not show any vibrational structure while the 3200 Å system contains a large number of discrete bands and vibrational analysis has been proposed for it.

The rotational analysis by Innes et. al [18] reveals that this system appears due to an $A, B_1, - X A$, transitions. Shashidhar & Rao [19] also studied the 2400 Å system in methyl pyrimidines. The electronic states of Azobenzene have been studied in great detail by Gupta, Sanyal, Goeletc [20,21] and other eminent workers [22,23] have studied the vibrational and electronic spectra of substituted pyrimidines and Azobenzene in details. Which would be of great help in removing ambiguities regarding assignments & geometrical structure of present molecules having biological & pharmacognostical importance [24]?

By considering the above facts the present study has performed on subjected molecule. The study have made on Vapor phase U.V. spectrum, complete electronic (ground & excited) assignments with detail interpretation with the help of various workers [24,25] have cited in this study.

MATERIAL–METHOD

The spec-pure chemicals 5-Bromo-2,4 (1H,3H)-pyrimidinedione [Here referred as 5,2,4- BP] were obtained from M/s ALDRICH Chemical comp. and used as such without further purification. However their purity was confirmed by elemental analysis and M.P. determination. The vapor phase U.V. spectra of compound was recorded BECKMAN DK-2A U.V. spectrograph in the range 250 - 370 NM. The procedure for analyzing the spectra was the same as described elsewhere [25].

RESULT OF ANALYSIS

Blout [8,9] have studied the structure of pyrimidine compounds & concluded that they have planar structure. The vapor phase UV of molecule is given in Fig.2.

The ground & excited state fundamentals observed in vapor phase U.V. spectra of molecule with (0,0) bands and systems are depicted in Table - 1.

The spectra of pyrimidine bases three or four band between 180 & 300 nm. In addition to this long wavelength $n-\pi^*$ transition, these bands also appear in many pyrimidine bases and presumably $\pi-\pi^*$ transitions. In pyrimidine a band is observed at 240 nm which corresponds to $A_1 - B_2$ transition and is derived from $A_{1g} - B_{2u}$ transition. Clark and Tinocco [26] suggested that the 210 & 220 nm bands of pyrimidine correspond to $A_{1g} - B_{1u}$ & $A_{1g} B_{1u}$ transitions for pyrimidine bases & showed the presence of-out-of-plane & in-plane transitions in pyrimidine bases.

The present molecules show two systems of bands in their respective spectra. The spectra of molecule are shown in Fig. –1. The wave no. of the vibronic band (both ground & excited state fundamentals) with their approximate intensities & probable assignments, analysis, with overtones & combination are given in Table –1. On the other hand the correlation of transitions found for present molecules with other molecules are given in Table –2.

The observed spectra of molecule 5,2,4-BP clearly shows only one system of bands. The very strong band named 0, 0 band are shown at 370370 cm^{-1} for system relating to $\pi-\pi^*$ system of pyrimidine and are correlated with other pyrimidine derivatives depicted in Table [1]. These are analogues to the system of bands studied by Uber [17] & Innes [18] in case of pyrimidine – d_6 . The ground & excited state values for 5,2,4 – BP are well detailed in Table -1. The ground & excited state bands are found at 133, 267, 400, 534, 667, 881, 935, 1069, 1203, 1337 1471, 1605, 1740, 1874, 2009, 2144, 2279 and 133, 266, 399, 532, 1327, 1459, 1491, 1715, 1855, 1987, 2119, cm^{-1} for $\pi-\pi^*$ system having (00) band at 370370 cm^{-1} . These values show close resemblance with the assignments & values of various U.V spectrum of substituted pyrimidines & benzenes. [27,28]

FIG: 1: Molecular structure of 5,2,4 – BHP

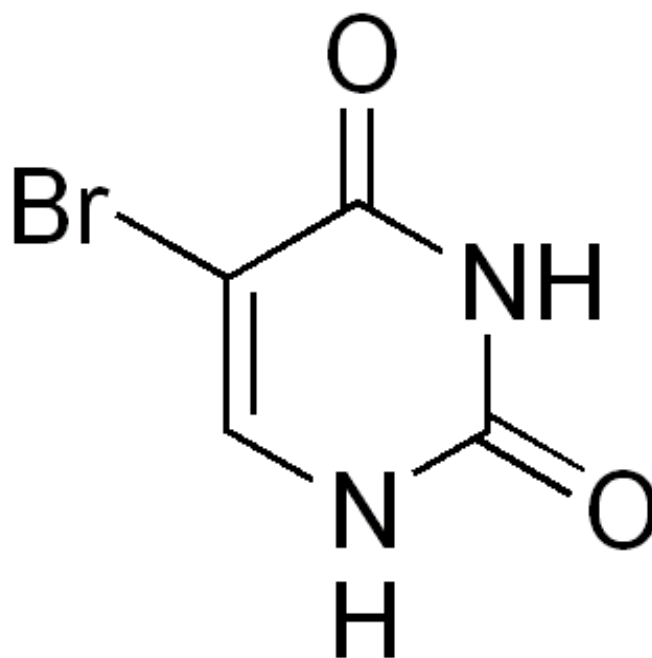


FIG: 2: U.V Spectra of 5,2,4 – BHP

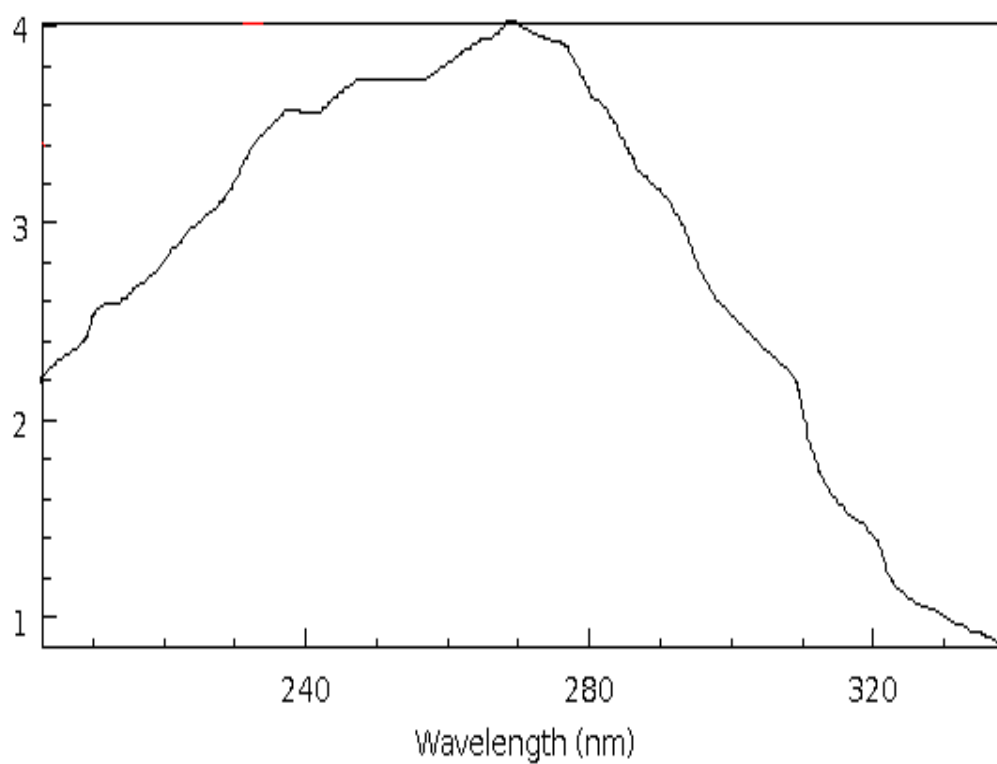


TABLE-1
ANALYSIS OF ELECTRONIC BANDS OBSERVED IN VAPOUR PHASE U.V. SPECTRA OF
5,2,4- BP (all values in cm^{-1})

Wave no. & intensity	Shift from (0,0) bands	Assignments
	$\pi-\pi^*$ system	
368299	0—2071	0—2071
368582	0—1788	0—1788
369244	0—1126	0—1126
369432	0—938	0—938
369526	0—844	0—844
369620	0—750	0—750
369714	0—656	0—656
369808	0—562	0—562
369902	0—468	0—468
369996	0—374	0—374
370089	0—281	0—281
370183	0—187	0—187
370277	0—93	0—93
370370 vvs	0,0	0,0
370464	0+94	0+94
370557	0+187	0+187
370650	0+280	0+280
370744	0+374	0+374
370837	0+467	0+467
370930	0+560	0+560
371023	0+653	0+653
371209	0+839	0+839
371302	0+932	0+932
371581	0+1211	0+1211
371859	0+1489	0+1489
372133	0+1763	0+1763
372320	0+1951	0+1951

TABLE – 2
Correlation of $n-\pi^*$ & $\pi-\pi^*$ transitions of 5,2,4- BP with similar molecules (all values in cm^{-1})

Sl No.	Molecules	$n-\pi^*$ Transition	$\pi-\pi^*$ Transition
1.	2, 3-Dichloroanisole +	—	35248

2.	2, 6- Dichloro anisole +	—	35868
3.	2-Amino-4-Chloro anisole+	—	33389
4.	Anisole+	47619	38461
5.	2-Amino-4-methyl pyrimidine +	43937	36101
6.	5-Ethyl-2- methyl pyrimidine +	47600	36640
7.	2-Hydroxy-5-Nitro pyridine+	48543	33333
8.	5-Bromo-2,4(1H,3H)-pyrimidinedione *	-----	370370

+. Ref – 29, * - Present work

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