

A study of solvent effect on electronic transition of 4,6-dihydroxy-5-methylpyrimidine using density functional theory

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Abstract— Heterocyclic organic compounds containing nitrogen, sulfur or oxygen (NSO_s) are an important class of groundwater contaminants related to the production and use of manufactured gas, heavy oils and coal tar. Nitrogen-containing cyclic organic molecules (N- heterocyclic) play important roles in terrestrial biology, for example as the nucleobases in genetic material. It has previously been shown that nucleobases are unlikely to form and survive in interstellar and circumstellar environments. The determination of the vibrational: infrared (IR), Raman spectra and electronic ultraviolet spectra are among the most important applications in computational chemistry. These spectroscopic investigation of N- heterocyclic compound tell about biotechnological, mineralogical and environmental monitoring property. In view of above we have selected a compound (4,6-dihydroxy-5-methylpyrimidine) which is biologically and environmentally very important.

Keywords—N-heterocyclic compound, electronic and vibrational spectroscopy, environment monitoring etc.

I. INTRODUCTION

Nitrogenous heterocyclic (N-heterocyclic) compounds are of immense concern from point view of environment and have potential application in manufacturing of dyestuffs, pesticides, agrochemicals and disinfectants. Due to their toxicity, mutagenicity and carcinogenicity, they constitute a danger for natural biogenic environment and severe odour potential. Furthermore, most of N-heterocyclic compounds are difficult to be degraded by microorganisms under aerobic and anaerobic conditions, and also have an adverse impact on the conventional biological wastewater treatment system for their toxicity to microbial communities. Nucleobases are nitrogen-containing heterocyclic aromatic compounds (N-heterocycles), found in the genetic material of all living organisms on Earth [1-3]. They can be divided into two groups according to their molecular structure: the purine derivatives (adenine, guanine, xanthine and hypoxanthine) and the pyrimidine derivatives (cytosine, thymine and uracil). In view of these it is clear that N-heterocyclic compounds

use in various applications such as quinoline derivatives uses as drugs (cancer, anti-malarial), fungicides, biocides, alkaloids, rubber chemicals, flavouring agents, catalyst, preservative, solvent for resins. Wound healing antibacterial, DNA binding, in vitro antioxidant activity [4-6], Benzoxazole derivatives are the structural isoesters of naturally occurring nucleotides such as adenine and guanine, which allows them to interact easily with the biopolymers of living systems and different kinds of biological activity have been obtained. It has been reported that they have shown low toxicity in warm-blooded animals [7,8]. Pyrimidine derivatives uses as drugs (antimicrobials, antitumours, antifungal thyroid drugs and leukemia), antiphotosynthetic herbicides, anti-inflammatory activity, agricultural chemicals, essentials constituent of RNA, alloxan, which is known for its diabetogenic action in a number of animals, pharmaceuticals etc [9-15]. Vibrational spectroscopy consists of Infrared and Raman spectroscopy, which are used for determining the chemical and biochemical components of materials and biological samples and their distributions there in. Today's competitive industrial environment requires manufactures to continuously strive to improve product quality whilst reducing manufacturing costs. Vibrational and electronic spectroscopy is well suited to process analysis and can thus help achieve these goals. Keeping these applications and importance of N-heterocyclic compounds, the present paper deals with 4,6-dihydroxy-5-methylpyrimidine.

II. EXPERIMENTAL DETAILS

Spectroscopic pure sample of 4,6-dihydroxy-5-methylpyrimidine was purchased from M/S Sigma Aldrich chemicals, U.S.A. The compound was used in their original form, the purity of the said compound was confirmed by elemental analysis and melting point determination. The ultraviolet spectra of this compound was recorded on Beckman Spectrophotometer model M-35 in the region 400-200nm using different polar and non-polar

solvents(viz.water,acetonitrile,dimethylsulphoxide,methanol). All the solvent used were of spectroscopic grade. The concentration of all the solution in all the cases was kept to be constant (8×10^{-3} gm/litre).

III. RESULTS AND DISCUSSION

The structural formula of the compound 4,6-dihydroxy-5-methylpyrimidine is shown in fig-(1). The electronic transition of the said compounds recorded in the different solvents (a) methanol (b) water (c) DMSO (c) acetonitrile are shown in fig (2). The vibrational:infrared spectra of the compound is shown in fig.(3)

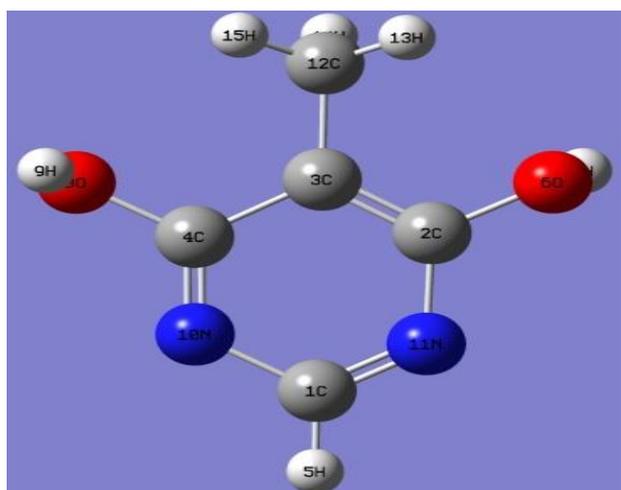


Fig.1. The molecular structure of 4,6-dihydroxy-5-methylpyrimidine

IV. ELECTRONIC SPECTRA

West[16] has suggested that changing of the solvent, effect the position of the band in the electronic spectra, which may be used to identify the band as $n-\pi^*$, $\pi-\pi^*$ and $n-\sigma^*$. Then $n-\pi^*$ transition of substituted pyrimidine occur at distinct bands in the region 340-300 nm. Yadav[17] suggested that $n-\pi^*$ transition corresponds to out-of-plane transitions while $\pi-\pi^*$ and $n-\sigma^*$ in-plane transitions.

V. SOLVENT EFFECT

Generally the solvents used in recording this spectrum are non-polar-one (like chloroform,hexane) or polar solvents (like methanol, acetonitrile, water, ethanol etc.). The band will be called blue shift or red shift. According to the band shift towards shorter wavelength or longer wavelength on changing the solvent from hexane to water, then $n-\pi^*$, transition are attributed to blue shift band while $\pi-\pi^*$ and $n-\sigma^*$ are attributed to red shift band. The amount of blue shift has been used as a measure of the strength of the H-bonding in ethanol, methanol,water, acetonitrile, dimethylsulphoxide and increase in transition energy. This energy required to weaken or break

the hydrogen bond. In the present investigation , the $n-\pi^*$ transition is blue shift in the compound with increasing polarity of the solvents. The red shift has been

Table 1: Theoretical absorption spectra of 4,6-dihydroxy-5-methylpyrimidine using TD-SCF/HF/6-31+(d,p) method in solvents acetonitrile, dimethylsulphoxide, water phase

Acetonitrile			Dimethylsulphoxide			Water			Assignments
R.I-1.3941			R.I-1.479			R.I- 1.3380			
DC-36.64			DC- 47.24			DC- 80.10			
λ (nm)	E(ev)	f	λ (nm)	E(ev)	f	λ (nm)	E(ev)	f	
249.339	4.9733	0.0047	249.219	4.9746	0.005	248.606	4.9866	0.0047	$\pi-\pi^*$
213.139	5.8178	0.063	213.134	5.8175	0.0686	212.687	5.8289	0.0643	$\pi-\pi^*$
199.531	6.2125	0.0031	199.626	6.2117	0.0024	199.714	6.2091	0.0023	$n-\sigma^*$

observed in the $\pi-\pi^*$ and $n-\sigma^*$ transitions in the said compounds with increasing polarity of the solvents are also given in table 1.

The attraction between the solute and solvents molecule will be more if the polarity of the molecule will be more, which results the system more stable. This with increasing the dielectric constant of the solvent, the ionizing polarity of the solute molecule will be increase. Hence, greater the polarity of the solvents, greater will be the degree of the solution.

where: λ - max wavelength, R.I- refractive index of solvent, DC- dielectric constant, E(ev)- excitation energies, f- oscillation strength

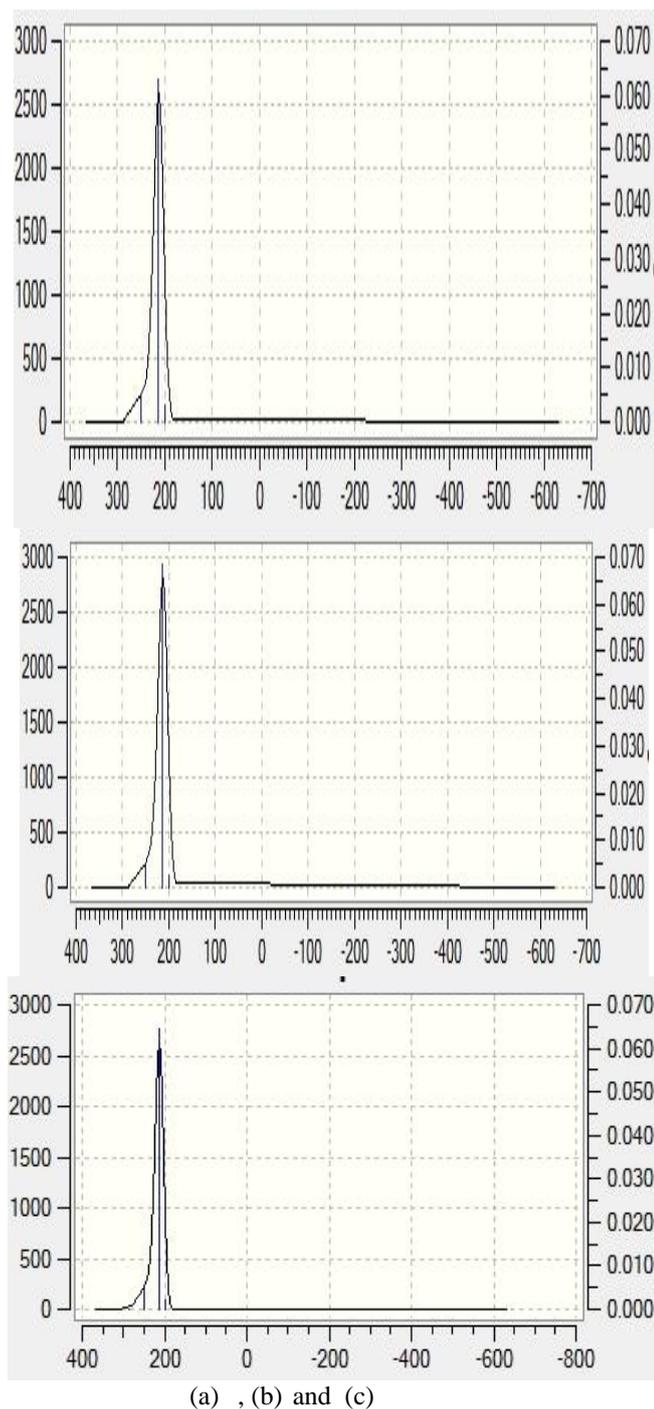


Fig.2.-Ultraviolet absorption spectra of 4,6-dihydroxy-5-methylpyrimidine in various solvents (a)Acetonitrile (b) Dimethylsulphoxide (c) Water

Due to present investigation , the $n-\sigma^*$ transition nearer at 210 nm in all solvents and $\pi-\pi^*$ transition nearer at 213 nm in all solvents have been taken to represent in-plane transition . No out-of plane transition has been found in present investigation.

VI. VIBRATIONAL SPECTRA: INFRARED SPECTRUM

Unlike ultraviolet spectrum which comprises of absorption bands from which a wealth of information can be derived about the structure of an organic compound. The absorption of infrared radiation of infrared radiations causes the various bands in the molecule to stretch and bend with respect to one another which is due to the changes in the vibrational and the rotational levels. Vibrational spectra depends upon two type of basic fundamental which are stretching and bending. Here assuming methyl & hydroxyl groups to behave as a single mass point, the symmetry element will be the molecular plane containing all atoms. The molecule will have only two types of vibrations(Planer & Nonplanar) and will be active in infrared spectrum[18]. Apart from these vibrations the fundamental frequencies associated with the different groups will also appear.

A. Ring Stretching

The ring stretching vibrations are very much prominent in the spectrum of benzene and its derivatives and are highly characteristic of the aromatic ring itself . Pyrimidine consist three isolated C-H stretching modes[19]. Some molecules are penta substituted so C-H stretching found which lies in 3100cm^{-1} - 3000cm^{-1} . Here the mode of vibration is found at 3087cm^{-1} . The spectra of pyrimidine shows the pair of absorption band at 1398, 1466, 1564, 1568cm^{-1} . [20]. These values find good support from the work of Goelet al.[21,22] & Job & Kailtra in substituted pyrimidines.

B. C-X Vibrations

In the present molecule methyl group is present so particular vibration is found for each stretching and bending. Sanyalet.al. [23] have assigned this mode at 1220cm^{-1} in 4,6-dihydroxy-2-methyl pyrimidine. Here this mode is found at 1280cm^{-1} Apart from these vibrations, it is interesting to note that some bands are identified in C=O region in the compound[24].

C. Methyl Group Frequencies

The molecule contains methyl groups hence there will be various modes under different stretching conditions. Bellamy[25] and others [26] have suggested that C-H stretching are found due to CH_3 group in the region 2800 - 3000cm^{-1} . Here, the present molecule contain vibrations at 2875cm^{-1} and the band has appeared at 1402cm^{-1} .

D. Hydroxyl Group Vibrations

Several workers [27] suggested that for molecules containing OH- group, the OH valance vibrations appears in the range 3500 - 3700cm^{-1} . In Phenol Evans[28] suggested that OH valance oscillates at 3528cm^{-1} . Here the molecule contain vibration at 3555 and 3590cm^{-1} which shows that function has a very characteristic shape[29].

VII. CONCLUSION

The structure of pyrimidine compounds found to be planner as in previous studies. The all fundamentals are studied with the

assignment of pyrimidine which are environmentally sensitive.

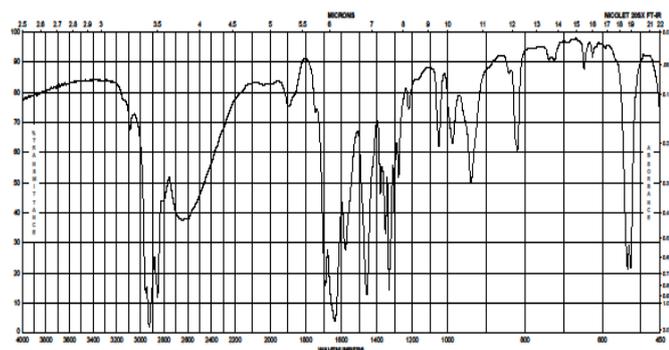


Fig.(3). Infrared Spectrum of 4,6-dihydroxy-5-methylpyrimidine.

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