

Effect of Ph and Ultraviolet Spectral Studies of 2,5- Dimethoxy Thio Phenol

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Abstract:- The ultraviolet spectra of 2,5-dimethoxy thio phenol has been recorded in the region 2000-3500 \AA . The electronic absorption spectra has been recorded in various solvents (viz. ethanol, methanol and water). The effect of substituents has been discussed. The effect of pH variation in ethanol solvent is also studied and discussed.

Keywords: electronic absorption spectra, pH effect and solvent effect.

INTRODUCTION

Spectroscopic studies of phenol and its derivatives received considerable attention in the recent years [1-3]. The studies of phenol derivatives have become quite interesting because they are the constituents of DNA & RNA and hence play a central role in the structure and properties of the nucleic acids. Also phenol derivatives like chlorophenol, aminophenol and marceptophenol etc. are widely used as drugs in certain diseases. Phenol and its derivative are extensively used as a solvent as a synthetic intermediate in analytical chemistry. So, the knowledge of the molecular structure, physio-chemistry properties and vibrational properties of phenol and its derivatives is helpful for a better understanding of their function in several biological processes and analysis of the complex systems. Sunderaganeshan [4] have shown that the phenol molecule has planer structure in the ground state and a quasi planer one in the excited state.

The absorption spectra of phenol and its derivatives have been predicted theoretically and practically by various workers [5,6] have found the evidence of the electronic transitions as $n - \pi^*$, $n - \pi^*$ and $n - \sigma^*$. This the detailed study of the electronic transitions of substituted phenols is of importance in order to check the presence of $n - \pi^*$, $\pi - \pi^*$ and $n - \sigma^*$. Thus the detailed study of the electronic transitions of substituted phenols is of importance in order to check the presence of $n - \pi^*$, $\pi - \pi^*$ and $n - \sigma^*$ transition [7,8].

In view of the above discussion, the ultraviolet spectra in different solvents (viz., ethanol methanol and water) of the 2,5-dimethoxy thio phenol is reported and discussed [5,9].

EXPERIMENTAL DETAILS

98% spec-pure grade sample of 2,5-dimethoxy thio phenol (abbreviated as 2,5-DMTP) was obtained from M/s Sigma Aldrich Chemic, West Germany and used as such without further purification. However, their purity was confirmed by elemental analysis and melting point determination [120-124 $^{\circ}$]. The experimental technique in the ultraviolet spectra of 2,5-DMTP was recorded on Beckman Spectrophotometer model-35 in the region 2000-3500 \AA . The spectra have been recorded in various solvents (viz. ethanol, methanol and water). The concentration of the solution in all the cases was kept constant (8×10^{-3} gm/liter). All the solvents used was of spectroscopic grade. The ratio of pure solvent was obtained at 9:1 by volume.

RESULTS AND DISCUSSION

The molecular structure of 2,5-dimethoxy thio phenol is given in fig.-1.

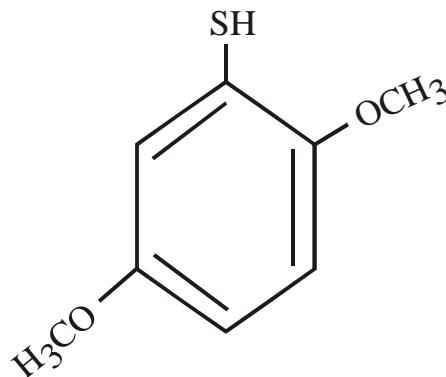


Fig. 1 : Molecular structure of 2,5-DMTP

The observed ultraviolet bands of said molecule are given in Table-1. The ultraviolet absorption spectra of the

said compound in different solvents (viz. ethanol, methanol and water) are shown in fig.2 and fig.-3.

ULTRAVIOLET SPECTRA

Some investigator [10-13] have suggested, in phenol the introduction of $-\text{OH}$ group replaced of H atom in benzene, exhibits a red shift in $\pi - \pi^*$ and $\text{n} - \sigma^*$ transition and blue shift in $\text{n} - \pi^*$ transition. In the present study, the UV spectra of the molecule 2,5-DMTP was recorded in different solvents (viz. ethanol methanol and water) but the band system which corresponds to

$^1\text{A} \longrightarrow ^1\text{U}$ transitions $\text{n} - \pi^*$ has been observed between 2950–3100 Å. The band system, which

corresponds to $^1\text{A}_{1g} \longrightarrow ^1\text{B}_{2u}$ transition ($\pi - \pi^*$) has been observed between 2300–2500 Å for the molecule 2,3-dihydroxy pyridine, while the band system which

corresponds to $^1\text{A}_{1g} \longrightarrow ^1\text{B}_{2u}$ transition has been observed between 2000–2100 Å for the molecule 2,3-dihydroxy benzaldehyde.

In view of this, the $\text{n} - \pi^*$ Transition observed at 2960 Å in 2,5-DMTP is taken to represent out-of-plane transition, while $\pi - \pi^*$ and $\text{n} - \sigma^*$ transition around 2240 and 2070 Å in-plane transition originated

from $\text{A}_{1g} \longrightarrow \text{B}_{2u}$ transition respectively. In

which the later one derives from $\text{A}_1 \longrightarrow \text{B}_1$ transitions [14,15].

SOLVENT EFFECT

The electronic spectra of a molecule when recorded in a solvent generally shift the band in comparison to those obtained in the vapour phase. This is called the solvents shift effect and is due to the weak physical interaction between solute and solvents atoms. This interactions may be generally classified into specific and non-specific solvents effect on the electronic state of solute. Specific solvents effects include ionisation charge transfer, aggregation phenomenon and hydrogen bonding of molecule. Non-specific effect is due to the depressive induction electro-state forces that may occur between solute and the surrounding solvents molecule. Solvent polarity effects the electronic transitions and this depends on whether the solute becomes more or less polar after excitation polar solvent. This change of charge distribution in the molecule and result increases delocalization [16-18] for $\pi - \pi^*$ transitions, both the ground and excited states are stabilized and the absorption moves towards longer wavelength. For

$\text{n} - \pi^*$ transitions, the ground state is more stabilized then the excited state and consequently absorption to the shorter wavelength.

In the present investigation, it is clearly observed that the $\text{n} - \pi^*$ transitions around 3100 Å is blue shifted in 2,5-DMTP with increasing polarity of the solvent (ethanol →

methanol → water) as shown in Table-2. It is evident that the blue shift has been observed in $\text{n} - \pi^*$ transitions of the molecule with increasing of refractive index of the solvents [66]. A red shift has been observed in the $\pi - \pi^*$ and $\text{n} - \sigma^*$ transitions around 2240 and 2070 Å in the 2,5-DMTP with increasing the polarity of the solvents (ethanol → methanol → water) which is identical to the trend reported for these transition in the literature value [9,11,19]. The shift is due to momentary polarization of the solvents by the transition dipole of the solute. The polarity of the solute also plays an important role in the electronic transition. In the present study the molecule 2,5-DMTP is non-polar, the shift of absorption spectra of slightly polar solute are predominantly due to the dipole–dipole interactions the solute and solvent in the ground and excited state respectively.

The hydrogen bonding will lower the energy of ground state more than that of excited state, which consequently increase the excitation energy in a blue shift. High dielectric constant leads to a higher transition energy and an emergence of a short wavelength band would be expected. During the present study in the said molecule, the shortest wavelength system 2070 Å has been observed in 2,5-DMTP [20-24].

Furthermore, the greater the polarity of the solvent, the greater the attraction between solute and solvent molecule. Thus, the system would be more stable [15]. Also with increasing dielectric constant of the solvent the ionising potentiality of the solute molecule is increased.

EFFECT OF PH VARIATION

The absorption spectra of the compound in different solvents at various pH are shown in Fig. [3] and in Table - 2. Yadav [15] suggested that in phenol, the substituent is of acidic nature like $-\text{OH}$, the molecule may exist in neutral, cationic or anionic form depending upon the pH of the solution, and the wavelength of the band around 3000 Å increases in the sequence neutral molecule → cation → anion [25,26].

In the present study, there is a blue shift in the position of entire band with the decrease in pH, the $\text{n} - \pi^*$ band is reported to shifted towards shorter wavelength [70]. These are in accordance with the trend observed during the present investigation [18,27].

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TABLE-2**ANALYSIS OF ELECTRIC SPECTRA OF 2,5-DMTP****(ALL VALUES ARE IN Å)**

Solvent	DC	RI	$n - \pi^*$	$\pi - \pi^*$	$n - \sigma^*$
Ethanol	25.0	1.3773	2960	—	—
Methanol	32.0	1.3362	2960	2240	—
Water	80.0	1.3380	2965	—	2070

Where, DC = Dielectric constant RI = Refractive index

TABLE-3**EFFECT OF PH VARIATION ON ULTRAVIOLET TRANSITION OF 2,5-DMTP****(ALL VALUES ARE IN Å)**

Solvent	$n - \pi^*$	$\pi - \pi^*$	$n - \sigma^*$
Ethanol	2780	—	—
Ethanol + HCl	2730	—	2080
Ethanol + NaOH	2680	2280	—

