

Effect of solvents and pH variation on electronic spectra of 4-bromo-2,6-dimethyl phenol

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ABSTRACT

Electronic spectra of 4-bromo-2,6-dimethyl phenol in polar solvents (ethanol, methanol and chloroform) have been recorded in the region 200 to 400nm. The effect of change of solvent on electronic transitions of this compound is explained. The effect of pH variation in ethanol solvent has also been studied.

Key words : Ultraviolet absorption spectra, electronic absorption bands.

INTRODUCTION

Phenol has been the subject of numerous studies, since it is a good model for the investigation of hydrogen bonding and the proton transfer in enzymes and other systems containing aryl alcohol¹. The theories of solvents effect on electronic spectra developed by authors²⁻⁴ are all based on the assumption of only non specific interactions among the solute and solvent molecule. The quantitative expressions furnished by these theories and the underlying approximation imply that the shift in solute band frequencies are governed only by the physical properties of solvent such as its refractive index, dielectric constant and its polar and non-polar nature etc. and are independent of its chemical nature⁵. The hydrogen bonding interaction of proton donating solvents such as alcohols with different solute is found to be the most important factor governing the shift of $n - \pi^*$ transition^{6,7}.

The specific solute-solvent interaction energies are estimated from the wavelength shift and analysed in the light of the functional groups in the solvent and solute molecule. Such a detailed study is expected to result in a better understanding

of the solvent effects on electronic spectra. Recently, B.S. Yadav *et al.*⁸ have reported the spectral studies of tri methyl aniline. In this paper, the ultraviolet spectra of 4-bromo-2,6-dimethyl phenol in various polar solvent (ethanol, methanol and chloroform) and the effect of pH variation and solvents on the $\pi - \pi^*$, $n - \pi^*$ and $n - \sigma^*$ transitions of this compound have been discussed.

EXPERIMENTAL

The spe-pure compound 4-bromo-2, 6-dimethyl phenol (M/s Aldrich Chemie, West Germany) was used for spectral studies. Its purity was confirmed by elemental analysis and melting point determination. The ultraviolet spectra of this compound was recorded in solvents (ethanol, methanol and chloroform) on UV-VIS double beam spectro-photometer, Model M-1601 in the region of 200 – 400 nm in liquid state. The solvents used for preparing the solution of the compound were of spectroscopic grade, The pH value of solution was measured with Systronic pH digital meter (model 335). This system was standardized at $\text{pH} \pm 0.1$, 7 ± 0.1 , 9 ± 0.1 at room temperature with the help of standard buffers. The concentration of the solution in all cases was kept

constant (8×10^{-3} gm/litre). The ratio of pure solvent and acid or alkali was maintained at 9:1 by volume.

RESULTS AND DISCUSSION

The molecular structure of 4-bromo-2,6-dimethyl phenol is shown in Fig. -1. The effect of solvents on the electronic transitions of this compound is given in Table -1. The effect of pH variation in solvent ethanol on the electronic transitions of this compound is given in Table -2. The near ultra-violet absorption spectra of this compound is shown in Fig. -2, while the absorption spectra of this molecule in ethanol solvent at different pH is shown in Fig. -3.

The spectra of phenol are as a whole similar to their corresponding hydrocarbon^{9,10}. According to Yadav *et al.*,⁸ the spectra of tri methyl aniline shows two intense band in the accessible ultraviolet region. One band appears at 292 nm and other at 225 nm in ethanol. The first band is

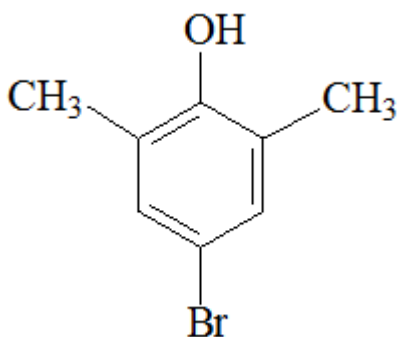


Fig. - 1: Molecular structure of 4-bromo-2,6-dimethyl phenol

probably an intermolecular charged transfer band due to a transition accompanied with a partial electron transfer from the electron donating methyl group to the electron accepting bromo group through the system of benzene ring. The steric effect on this band was studied by Arnold & coworkers¹¹.

The band observed at 238 nm corresponds to $A_1 \rightarrow B_2$ transition and derived from $A_{1g} \rightarrow B_{1u}$ transition on lowering the symmetry from $D_{6h} \rightarrow C_{2v}$ ^{8,9}. According to Clark and Tincoo¹² band at 210 nm and 200 nm corresponds to $A_{1g} \rightarrow B_{1u}$ and $A_{1g} \rightarrow A_{1u}$ transitions respectively. The bands are weak as the said transitions are forbidden but they are understood to occur as a result of coupling with variation of suitable symmetry^{11,13}.

In the present study, a blue shift of $n - \pi^*$ bands observed in 4-bromo-2, 6-dimethyl phenol on increasing the polarity of solvent (ethanol $\rightarrow$ methanol $\rightarrow$ chloroform) is given in Table -2. The blue shift of $n - \pi^*$ transition is due to the stabilization of ground state by hydrogen bonding in solvents and increase in transition energy, which is required to break or weaken the hydrogen bond¹⁴. The blue shift with increasing the polarity of solvents (ethanol $\rightarrow$ methanol $\rightarrow$ chloroform) is useful means of recognizing $n - \pi^*$ transition. From Table -1, it is apparent that a red shift has been observed with increase of refractive index of solvent which is similar to the behaviour observed in literature^{15,16}.

The $p - \pi^*$ transition undergoes a red shift for 4-bromo-2, 6-dimethyl phenol on increasing the polarity of solvents (ethanol $\rightarrow$ methanol $\rightarrow$ chloroform) shown in Table -1. This may be attributed to the monetary polarization of the solvents by transition dipole of solute¹⁷⁻²¹.

Table - 1. Effect of solvents on electronic transition of 4-bromo-2, 6-dimethyl phenol (All values are in nm)

Solvent	R.I.	DC	$n - \pi^*$	$\pi - \pi^*$	$n - \sigma^*$
Ethanol	1.3773	25	282	230	207
Methanol	1.3662	32.5	281	231	208
Chloroform	1.458	4.5	280	239	-

R.I. = Refractive index, DC = Dielectric constant

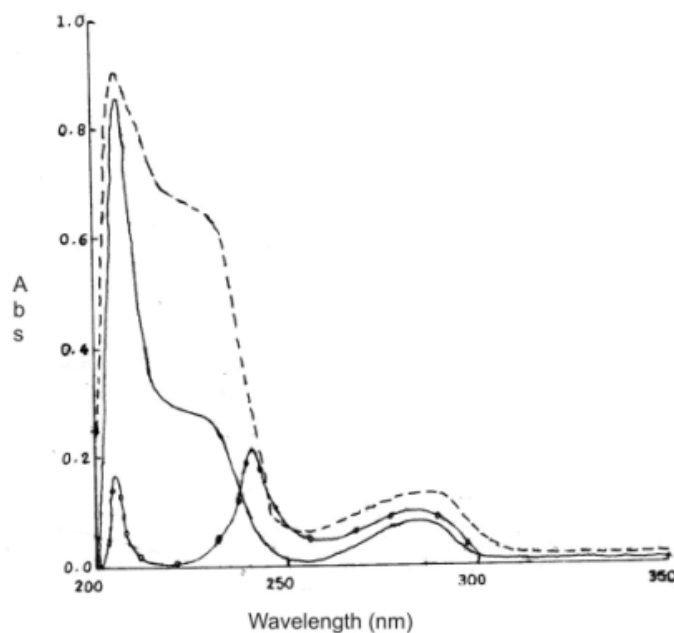


Fig. - 2: Ultraviolet absorption spectra of 4-bromo-2, 6-dimethyl phenol in (--) ethanol, (-) methanol and (o-o-o)chloroform

A red shift in $n - \sigma^*$ transition is observed in 4-bromo-2, 6-dimethyl phenol on increasing the polarity of solvents (ethanol $\rightarrow$ methanol $\rightarrow$ chloroform) is shown in Table -1. It is due to the presence of methyl group which enhances its hydrogen bonding capacity which is similar to the behaviour observed in literature¹⁸.

Effect of pH variation

Since the interpretation of spectral measurements to a considerable extent mainly depends on the choice of sites of localization of protons, the question of possible effect of pH variation on electronic transitions of compounds under study is very important.

In present study, there is a blue shift in the position of entire band with the decrease in pH, the $n - \pi^*$ band is reported to shifted towards shorter wavelength in acidic solution by many coworkers¹⁷. Silverstein¹⁰ have suggested a blue shift in $n - \pi^*$ band with the addition of acid solution due to the binding of non-bonded electrons by protonation. In accordance with the above, we have observed a red shift in $n - \pi^*$ band with the addition of alkali in the aqueous solution of 4-bromo-2, 6-dimethyl phenol shown in Fig.-3. Yadav *et al.*,¹⁴ have observed a red shift with the increase in pH in aniline. On increasing pH, a slight red shift in $p - \pi^*$ band of this compound is observed which is similar to the behaviour observed in literature¹⁸.

Table - 2: Effect of pH variation on electronic transition of 4-bromo-2, 6-dimethyl phenol (All values are in mm)

Solvent	pH value	$n - \pi^*$	$\pi - \pi^*$	$n - \sigma^*$
Ethanol	8.81	282	230	207
Ethanol + HCl	2.93	280	230	208
Ethanol + NaOH	11.98	288	232	207

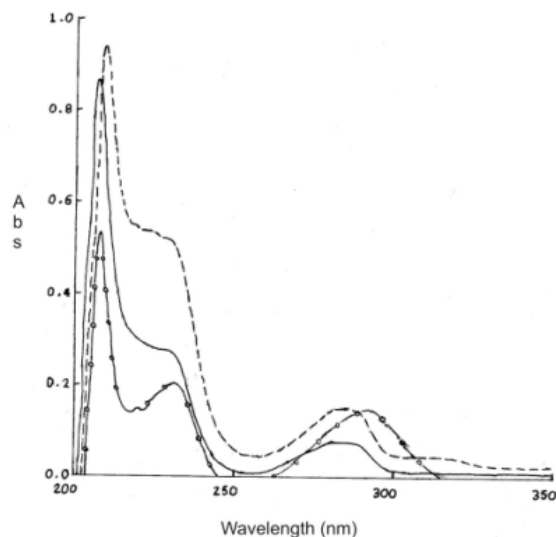


Fig. - 3: Ultraviolet absorption spectra of 4-bromo-2, 6-dimethyl phenol in (--) neutral, (-) acidic and (o-o-o) alkaline medium

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