

# Effect of Solvent on the UV Absorption Spectra of Benzalaniline Derived from Furfuryl Amine

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**Abstract**— The effects of solvents have been studied through the absorption spectra of benzalaniline in the range of 200-400 nm. With the help of Kamlet equation the effect of solvent polarity and hydrogen bonding on the absorption spectra are interpreted and the results are discussed.

**Key words:** Benzalaniline, Absorption, Furfuryl Amine, UV Spectra

## I. INTRODUCTION

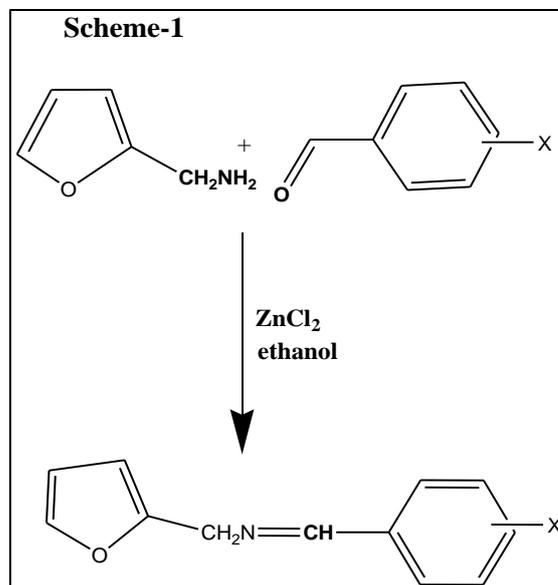
The solvatochromic shift can provide vital information regarding charge distribution in the solute molecule, geometry of the molecule, nature of transition in the ground and excited states [1-5]. These effects are predominantly electrostatic and may of induced dipole – induced dipole, dipole-dipole or hydrogen bonding [6] types. The effect of substitution on the intensities and absorption maxima has been the subject of considerable experimental and theoretical study [7-11]. Although far more attention have been paid to study and interpret the UV absorption spectra of simple amides but only significant work has been carried out in this direction for benzalaniline. So the present investigation is aimed to study the effect of substituent and solvent on the electronic absorption spectra of some *ortho*, *meta* and *para*-substituted benzalaniline.

## II. EXPERIMENTAL SECTION

All the reported melting points were taken in open capillaries and are uncorrected (Table.1). In all the cases, the progress of the reaction is monitored by TLC method, which revealed that the reactions were proceeding smoothly in the expected pathway. Mass spectra were recorded on Varian GC/mS# in using methanol as solvent

### A. General procedure for the preparation of benzalaniline

The benzalaniline were prepared[12] by refluxing equimolar quantities of methoxy substituted benzaldehyde and Furfuryl amine in alcohol for about 2 to 3 hrs. The resulting solution was cooled and poured into the cold water. The precipitated benzalaniline were filtered, washed dried and recrystallized from alcohol.



where X = H, p-OCH<sub>3</sub>, m-OCH<sub>3</sub>, p-NO<sub>2</sub>, m-NO<sub>2</sub>, p-CH<sub>3</sub>, m-CH<sub>3</sub>, p-Cl, m-Cl, p-Br.

## III. RESULTS & DISCUSSION

### A. Effect of solvents on the ultraviolet absorption spectra

It is well known that when an excited state has considerable charge separation relative to its ground state, the absorption is shifted to longer wavelength by increasing the polarity of the solvent. The solvent effect that takes place in any electronic transition is represented below (Fig. 1).

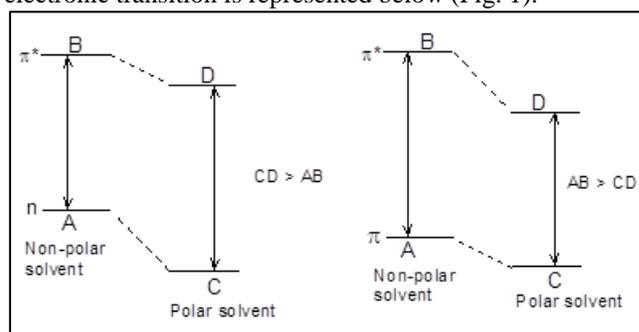


Fig1: Solvent effect in electronic transition

As one of the electronic transitions in all the Benzalaniline is  $\pi^* \leftarrow \pi$ , this transition is expected to shift its wavelength of maximum absorption to longer wavelength by increasing the polarity of the solvent. Hence the ultraviolet absorption spectra of the Benzalaniline derived from furfuryl amine were recorded in hexane and in ethanol-water mixtures of varying dielectric constant. The absorption maximum in hexane is considered that due to electronic transition from a non-solvated ground state to a non-solvated excited state. The difference in absorption maxima between those in alcohol-water mixtures and those in hexane is a direct measure of the excited state stabilization energy of the

Benzalaniline under investigation in various percentage of alcohol-water mixture. The  $\Delta\lambda_{\max} = [\lambda_{\max}(\text{ethanol-water}) - \lambda_{\max}(\text{hexane})]$  values and the dielectric parameters of the solvent mixture are given in Table 1.

Ethanol (%) in ethanol-water	$\lambda_{\max}$ (nm)	$\Delta\lambda_{\max}$ (nm)
100	338.60	21.2
90	339.80	22.4
80	341.80	24.4
70	342.00	24.6
60	343.00	25.6
50	343.80	26.4
40	344.80	27.4

n - Hexane = 317.40 nm

Table 1: Absorption maxima for benzalaniline

The plots of  $\Delta\lambda_{\max}$  versus  $\epsilon$ ,  $1/\epsilon$  and  $f(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1}$ ,

Kirkwood<sup>13</sup> function of dielectric constant are shown in Figs. 6-8. In all the plots there is a perfect linearity between the stabilization energy and the dielectric constants of the alcohol-water mixtures establishing the fact that the stabilization energy is increased by solvation of the excited state. Dielectric constant of various percentage of ethanol-water mixtures are given in Table 2

Ethanol (%) in ethanol-water	$\epsilon$	$1/\epsilon$	$f(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1}$
100	24.30	0.041	0.469
90	29.80	0.033	0.475
80	35.48	0.028	0.479
70	41.07	0.024	0.482
60	46.66	0.021	0.484
50	52.25	0.019	0.486
40	57.84	0.017	0.488

Table 2: Dielectric constant of various percentage of ethanol-water mixtures

As there is perfect correlation between the stabilization energy of the excited state and dielectric constant of the medium, it was thought of great interest to see if any correlation exists between stabilization energy of the excited state and dielectric constant of the medium by varying the alcohols themselves.

Hence the ultraviolet absorption spectra of the Benzalaniline was recorded in hexane and in various alcohols of varying dielectric constants such as 1-butanol, 2-butanol, 2-propanol, 2-methyl-2-propanol, benzyl alcohol, methanol, ethanol and 1-propanol. As mentioned earlier the difference in absorption maxima between those in hexane and those in various alcohols is a direct measure of excited state stabilization energy of Benzalaniline under investigation in various alcohols. The absorption maxima  $\lambda_{\max}$ ,  $\Delta\lambda_{\max}$  and  $\log \Delta\lambda_{\max}$  in various solvents are presented in Table 3.

S. No.	Solvent	$\lambda_{\max}$ (nm)	$\Delta\lambda_{\max}$ (nm)	$\log \Delta\lambda_{\max}$ (nm)
1.	1-Butanol	339.60	22.20	1.3464
2.	2-Butanol	338.20	28.80	1.4594
3.	2-Propanol	336.40	19.00	1.2788

4.	2-Methyl-2-propanol	337.00	19.60	1.2923
5.	Benzyl alcohol	346.00	28.60	1.4564
6.	Methanol	337.00	19.60	1.2923
7.	Ethanol	339.80	22.40	1.3502
8.	Propanol	340.60	23.20	1.3655

(n-Hexane = 312.40 nm)

$$\Delta\lambda_{\max} = (\lambda_{\max} \text{ ethanol} - \lambda_{\max} \text{ hexane})$$

Table 3:  $\lambda_{\max}$ ,  $\Delta\lambda_{\max}$  and  $\log \Delta\lambda_{\max}$  of benzalaniline in various alcohols

The solvent effect is best interpreted in terms of the following properties:

- 1) the dielectric behaviour
- 2) the ability of the medium to solvate
- 3) the ability of protic solvent to form hydrogen bond with negative end of the dipole.

The Kirkwood function<sup>13</sup> of the dielectric constant

$$f(\epsilon) = \frac{\epsilon - 1}{2\epsilon + 1}$$

is a suitable measure of (a) while (b) and (c) together are governed mainly by the polar effect of the alkyl group of the alcohol, suitably measured by the Taft polar substituent constants<sup>15</sup>  $\sigma^*$  the solvent parameter employed are compiled in Table 4.

S. No.	Solvent	$\epsilon$	$f(\epsilon)$	$\sigma^*$	$E_s$	$n\gamma_H$
1.	1-Butanol	17.1	0.4574	-0.13	0.39	2
2.	2-Butanol	15.8	0.4540	-0.21	1.13	3
3.	2-Propanol	18.3	0.4601	-0.19	0.47	0
4.	2-Methyl-2-propanol	10.9	0.4410	-0.30	1.54	0
5.	Benzyl alcohol	13.1	0.4448	0.215	0.38	0
6.	Methanol	32.0	0.4774	0.00	0.00	0
7.	Ethanol	24.3	0.4698	-0.10	0.07	0
8.	1-Propanol	20.1	0.4636	0.155	0.36	3

Table 4: Solvent parameters for alcohols

Since the excited state in all the Benzalaniline involve charge separations, one might expect that the excited state will be stabilized by increasing the polarity of the alcohols. Hence it was attempted to see if any correlation existed between  $\log \Delta\lambda_{\max}$  versus  $\epsilon$ ,  $1/\epsilon$  and  $f(\epsilon)$ . In all the cases the correlations were extremely poor and are shown in Table 4

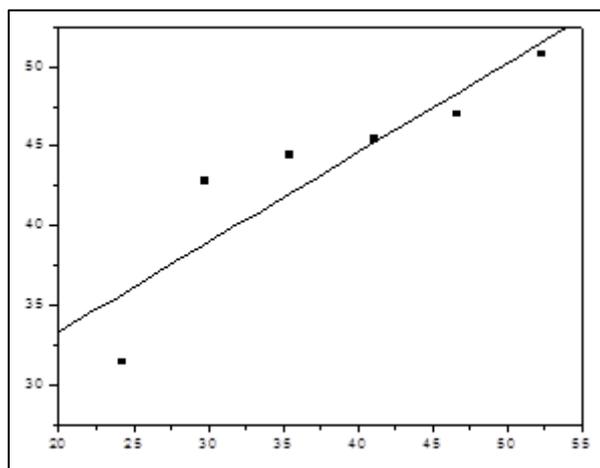


Fig. 2: The plot of  $\lambda_{\max}$  of substituted benzalaniline Vs  $\epsilon$

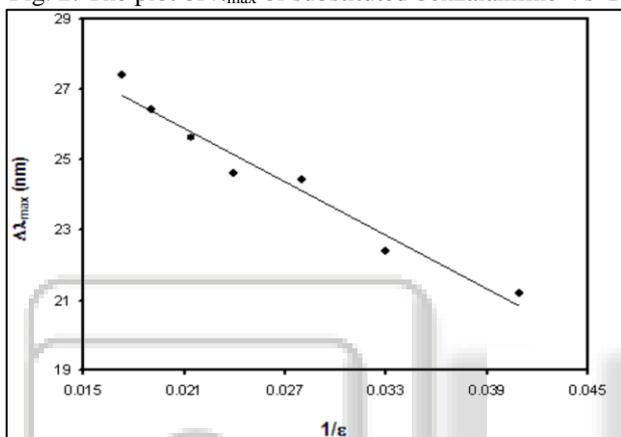


Fig. 3: Plot of  $\lambda_{\max}$  of substituted benzalaniline versus  $1/\epsilon$

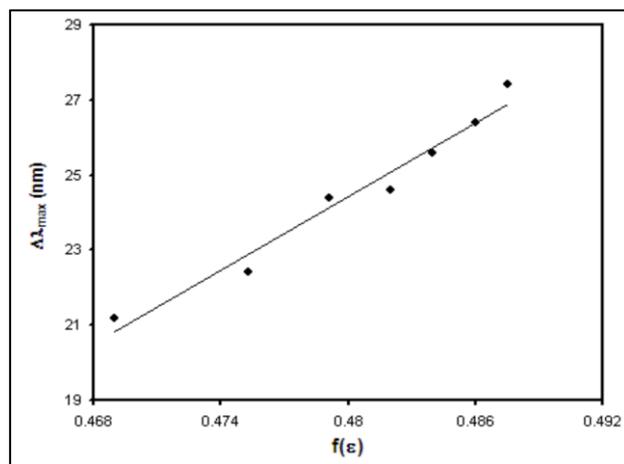


Fig. 4: Plot of  $\lambda_{\max}$  of substituted benzalaniline versus  $f(\epsilon)$

Later an attempt was made to improve the correlation by employing  $\sigma^*$ , the polar substituent constants of the alcohols. In these cases also the correlation were miserable as shown in Table 4 (S. No. 1) and the corresponding calculated  $\log \Delta\lambda_{\max}$  values are given in Table 5. It (Table 8) indicates very clearly that it is not possible for any single parameter equation to account for the observed results and it may be explained with the help of a multi parameter equation.

In this endeavor correlations have been sought with  $E_s$ ,  $n\gamma_H$ ,  $f(\epsilon)$  and  $\sigma^*$  values generating equations (S. No. 2, 3, 4) which are presented in Table 5. In these cases also the correlations are very poor, though there has been a slight improvement in some cases.

S. No.	Correlation	Correlation equation	Solvent
1.	$\Omega\iota\tau\eta \sigma^*$	$\log \Delta\lambda_{\max} = 1.3344 + 0.109 \sigma^*$ $\rho = 0.168, v = 8, \Sigma\Delta = 13.980$	
2.	$\Omega\iota\tau\eta \sigma^* \text{ ανδ } \phi(\epsilon)$	$\log \Delta\lambda_{\max} = 1.2965 + 0.0294 \sigma^*$ $+ 0.1926 \phi(\epsilon)$ $\rho = 0.571, v = 8, \Sigma\Delta = 0.066$	1-Butanol, 2-Butanol, 2-Propanol,
3.	$\Omega\iota\tau\eta \sigma^* E_s \text{ ανδ } n\gamma_H$	$\log \Delta\lambda_{\max} = 1.2941 + 0.0501 \sigma^*$ $- 0.04004 E_s + 0.17606 n\gamma_H$ $\rho = 0.610, v = 8, \Sigma\Delta = 0.079$	2-Methyl-2-propanol, Benzyl alcohol, Methanol, Ethanol, 1-Propanol
4.	$\Omega\iota\tau\eta E_s, \phi(\epsilon) \text{ ανδ } n\gamma_H$	$\log \Delta\lambda_{\max} = 1.2955 + 0.03158 E_s$ $+ 0.121 n\gamma_H + 0.0238 \phi(\epsilon)$ $\rho = 0.548, v = 8, \Sigma\Delta = 0.0844$	

Table 5: Correlation equation with  $\sigma^*$ ,  $f(\epsilon)$ ,  $E_s$  and  $n\gamma_H$  constant

Kamlet *et al.*<sup>16</sup> proposed a general solvation equation which explains the effect of solvent polarity and hydrogen bonding which takes the form

$$\log \lambda_{\max} = v_0 + S\pi^* + a\alpha + b\beta \quad (6)$$

This equation (6) is called as linear solvation energy relationship (LSER). Here  $\alpha$ ,  $\beta$  and  $\pi^*$  are solvatochromic

parameters (Appendix I) and  $a$ ,  $b$  and  $S$  are solvatochromic co-efficients. The variable  $\alpha$  is a measure of the solvent hydrogen bond donor (HBD) acidity and describes the ability of a solvent to donate a proton in a solvent-to-solute hydrogen bond. The variable  $\beta$  is a measure of the solvent hydrogen bond acceptor (HBA) basicity and describes the ability of a

solvent to accept a proton in a solute to solvent hydrogen bond.

The multiple linear regression analysis of the spectroscopic data for benzaniline for  $\pi \rightarrow \pi^*$  transition in seventeen different solvents (Table 6) were carried out using the equation 1. The results of the regression analysis are given below.

$$\begin{aligned} \log \lambda_{\max} &= h + S\pi^* + a\alpha + b\beta \quad (1) \\ &= 2.505 + 0.024231\pi^* + 0.01184\alpha + 0.0030\beta \\ &(\pm 0.00258) (\pm 0.045) (\pm 0.0036) + (\pm 0.004) \\ n &= 17; R = 0.910; SE = 0.049 \end{aligned}$$

In  $\pi \rightarrow \pi^*$  transition of benzaniline the positive sign of co-efficient 'S' and 'b' indicates a hypsochromic shift with both increasing the solvent polarity and hydrogen bond acceptor basicity ( $a/S = 0.4886$ ;  $b/S = 0.1238$ ). The positive sign of co-efficient 'a' indicates a hypsochromic shift with increasing solvent hydrogen bond donor acidity.

Absorption of benzaniline for  $\pi \rightarrow \pi^*$  transition are compared with solvent parameters  $E_T$  (30)<sup>17, 18</sup> (Table 10). But the correlation of  $\lambda_{\max}$  of benzaniline with  $E_T$  (30) values are poor ( $r = 0.8481$ ;  $A = -51.71$ ;  $B = 20.645$ ;  $n = 18$ ). The poor correlation may be due to presence of hydrogen bonding and change in geometry during excitation.

S. No.	Solvents	$\lambda_{\max}$ (nm)	$\log \lambda_{\max}$
1.	Methanol	336.17	2.5276
2.	2-Methyl-propan-2-ol	336.97	2.5276
3.	Propan-1-ol	350.60	2.5322
4.	Benzyl alcohol	346.02	2.5391
5.	Butan-1-ol	339.60	2.5309
6.	Butan-2-ol	338.06	2.5290
7.	Propan-2-ol	336.43	2.5269
8.	Ethanol	339.78	2.5312
9.	Dioxane	327.79	2.5156
10.	DMSO	341.97	2.5340
11.	Ethyl acetate	326.81	2.5143
12.	n-Hexane	317.31	2.5016
13.	Acetonitrile	328.78	2.5169
14.	Cyclohexane	320.04	2.5052
15.	Pyridine	335.43	2.5256
16.	Triethylamine	327.08	2.5146
17.	Xylene	330.52	2.5192
18.	Carbon tetrachloride	325.79	2.5129

Table 6: Absorption maxima for benzaniline in polar and non-polar solvents

S.NO	CORRELATION	CORRELATION EQUATION	SOLVENT
1	With $\sigma^*$	$\log \Delta\lambda_{\max} = 0.837 + 0.927 \sigma^*$ $r = 0.112, n = 8,$ $SD = 0.7955$	1-Butanol, 2-Butanol, 2-Propanol, 2-Methyl-2-propanol, Benzyl alcohol, Methanol, Ethanol, 1-Propanol
2	With $\sigma^*$ and $f(\epsilon)$	$\log \Delta\lambda_{\max} = 12.62 + 4.037 \sigma^*$ $+ 24.60 f(\epsilon)$ $r = 0.185, n = 8,$ $SD = 0.861$	
3	With $\sigma^*$ , $E_s$ and $n\gamma H$	$\log \Delta\lambda_{\max} = 3.29 + 0.23 \sigma^* - 4.66 E_s - 0.344 n\gamma H$ $r = 0.693, n = 8, SD = 0.707$	
4	With $E_s$ , $f(\epsilon)$ and $n\gamma H$	$\log \Delta\lambda_{\max} = 1.07 - 0.444 E_s + 208 n\gamma H - 0.35 f(\epsilon)$ $r = 0.701, n = 8, SD = 0.708$	

Table 2: Correlation equation with  $\sigma^*$ ,  $f(\epsilon)$ ,  $E_s$  and  $n\gamma H$  constant

The effects of solvent polarity and hydrogen bonding have been studied in the present series of compound by taking the unsubstituted compound as the representative. The spectra are recorded in eighteen different solvents and the data are given in Table 3. The above said effects are interpreted by means of linear solvation energy relationship (LSER) concept proposed by Kamlet *et al.*[12] which explains the effect of solvent polarity and hydrogen bonding which takes the form

$$\log \lambda_{\max} = \gamma_0 + S\pi^* + a\alpha + b\beta \quad (1)$$

Hence  $\alpha$ ,  $\beta$  and  $\pi^*$  are solvatochromic parameter and  $a$ ,  $b$  and  $S$  are solvatochromic co-efficients. The variable  $\alpha$ - is a measure of the solvent hydrogen bond donor (HBD) acidity and describes the ability of solvent to donate a proton in a solvent to solute hydrogen bond. The variable  $\beta$  is

measure of the solvent hydrogen bond acceptor (HBA) basicity and describes the ability of a solvent to accept a proton in a solute to solvent hydrogen bond.  $\pi^*$  is an index of the solvent dipolarity/polarisability which is a measure of the ability of the solvent to stabilize a charge or dipole by virtue of its dielectric effect. The multiple linear regression analysis of spectroscopic data for benzaniline for  $\pi \rightarrow \pi^*$  transition in eleven different solvents were carried out using eqn. (2).

$$\begin{aligned} \log \lambda_{\max} &= h + S\pi^* + a\alpha + b\beta \quad (2) \\ &2.299 + 0.1648 \pi^* + 0.033 \alpha + 0.062 \beta \\ n &= 11 R = 0.910 SE = 0.024 \end{aligned}$$

The positive sign of co-efficient 'S' and  $b$  indicates a hypsochromic shift with both increasing the solvent polarity and hydrogen bond acceptor basicity and the sign of 'a' indicates a hypsochromic shift with increasing solvent

hydrogen bond donor acidity. The  $\lambda_{\max}$  values for the unsubstituted compound in eighteen different solvents are compared with solvent parameter ET (30) (Table 3). But the correlation is not fair ( $r = 0.8481$ ). This poor correlation may be due to the presence of hydrogen bonding and change in geometry during excitation.

#### IV. CONCLUSION

The UV absorption spectra of benzalaniline were recorded in ethanol and hexane. There is no indication of  $\pi^* \leftarrow n$  transition in any of the cases. Only a fair correlation is obtained between  $\lambda_{\max}$  and  $\sigma$  as well as  $\sigma^+$ . The solvent effect on  $\pi^* \leftarrow \pi$  transition is studied in ethanol solution by changing the dielectric constant of the medium. Good correlation is obtained when  $\log \lambda_{\max}$  is plotted against  $\epsilon$ ,  $1/\epsilon$  and  $f(\epsilon)$ . Similar correlation is made by varying alcohol themselves. In these cases the correlation between  $\log \lambda_{\max}$  and  $\epsilon$ ,  $1/\epsilon$  and  $f(\epsilon)$  were very poor but better correlations were made when multi parametric equations are used. The effects of hydrogen bonding and solvent polarity on the unsubstituted compound in different solvents have been studied by using LSER equation.

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