

## Research Article

## Solvent effects on absorption spectra of (E)-1-(2,3)-dihydrobenzo[b][1,4]dioxin-7-yl)-3-phenylprop-2-en-1-one(DHP)

Subramanian Srinivasan\* and Srinivasan Thirumalmurugan

Department of Chemistry, Annamalai university, Annamalainagar. – 608002, Tamilnadu, India

**Abstract**

The (E)-1-(2,3)-dihydrobenzo[b][1,4]dioxin-7-yl)-3-phenylprop-2-en-1-one (DHP) have been prepared and characterized by <sup>1</sup>H NMR, and IR spectroscopy. UV spectra of DHP have been recorded in protic and aprotic solvents in the range of 200 to 600 nm. The photophysical behavior of dissolved chalcone depends on the nature of the environment i.e., intensity, shape, and wavelength of the absorption band of DHP. In all the spectra the principle absorption is only  $\pi \rightarrow \pi^*$  transition occurs. The effects on the absorption spectra of this new chalcone were interpreted by correlation of absorption frequencies with solvent parameters. The solute-solvent interactions were clarified on the basis of Linear Solvation Energy Relation Ships concept (LSER) proposed by Kamlet –Taft.

**Keywords:** 1,4-benzodioxo unsaturated ketones, chalcones , solvent effects of chalcones

**\*Correspondence**

Author: Subramanian Srinivasan  
Email: drssvasan16@rediffmail.com

**Introduction**

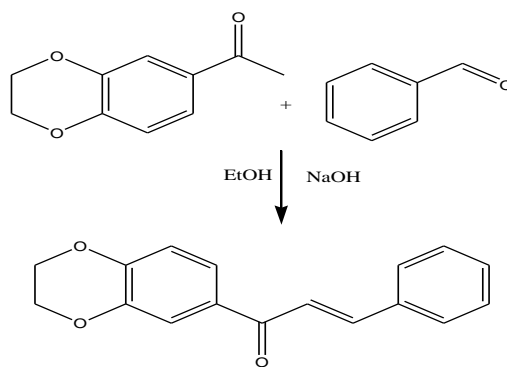
Chalcones are open chain flavonoids with two aromatic rings attached by a carbonyl group and  $\alpha$ ,  $\beta$ -unsaturated carbon atoms [1-3]. Chalcones are all well-known intermediates for synthesizing different types of heterocyclic compounds such as flavonoids which are naturally occurring in plants [4, 5],  $\alpha$ ,  $\beta$ -Unsaturated ketones have attracted increasing attention due to their numerous pharmacological properties such as anticancer activity, cytotoxicity, anti-inflammatory, analgesic and antipyretic behavior [6]. Some of them are potential antibacterial, antifungal and anti-ulcer agents [7]. They are also very useful intermediates in organic synthesis heterocyclic and organometallic compounds [8]. The present investigation is targeted to study the solvent effects through spectra structure relationship and structure solvent relationship. Structural, insect antifeedant activities non-linear optical behavior analysis of some novel chalcones has been studied by Srinivasan et.al [9-14]. A number of workers [15-17], have reviewed and critically examined the correlation of substituent constants with ultraviolet absorption frequencies. They observed that in these correlations, many difficulties are involved both in interpretation and accuracy of measurement. By means of dual substituent parameter (DSP) treatment using various combinations [18] of the following constants, i.e.,

$$\begin{aligned} K &= (D-1)/(2D-1); M=(n^2-1)/(2n^2+1) \\ J &= (D-1)/(D+2); H=(n^2-1)/(n^2+2); \\ N &= J-H. \end{aligned}$$

Brownlee and Topsom [19] and Topsom [20] convincingly showed that previously claimed simple relationship between frequency shifts and substituent parameters are mostly unfounded when the substituents were part of the studied chromophoric system. When the substituent's being varied were not part of the chromophoric system, however, it was shown that good correlations were possible. In the recent past, several reports were available on the correlations between ultraviolet absorption frequencies with substituent parameters [21, 22].

**Materials and Method**

DHP was synthesized by mixing stoichiometric amounts 1,4-benzodioxo acetophenone 0.001M and benzaldehyde the 0.001M molar ratio of (1:1) (**Scheme 1**) the reactant were dissolved in ethanol, thoroughly mixed using magnetic stirrer(1h) and 10% sodium hydroxide solution was added drop by drop for 3 minutes at 35°C. After stirring 3hr the contents of the flask were purified by recrystallization process using ethanol as a solvent (yield90%). The completeness of the reaction was monitored by thin layer chromatography.



Scheme 1

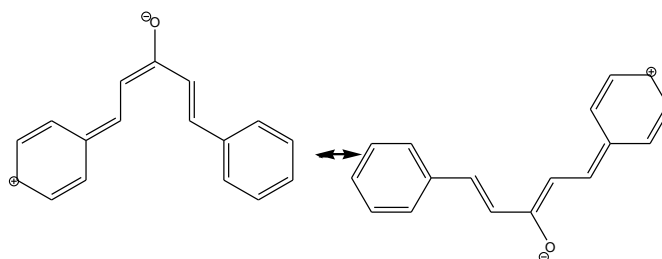
### Compound analysis

The IR spectrum of compound has some common features as far as chalcones are concerned. The sharp absorption band appeared at  $1653\text{ cm}^{-1}$  is because of the C=O group, while those arising at  $1570\text{ cm}^{-1}$  is due to the CH=CH functional. The purity and composition of DHP was checked by  $^1\text{H NMR}$  spectroscopy in  $\text{CDCl}_3$ . The triplet observed at 4.26 ppm assigned to the methylene proton in 1,4 phenyl ring. In the case of the phenyl ring and 1,4-phenyl ring, aromatic proton signals lying in the range of 6.97 ppm.

The signals observed at 7.741 (d  $^1\text{H}$ ;  $J = 15.6\text{ Hz}$ ) and 7.452 (d  $^1\text{H}$ ;  $J = 15.6\text{ Hz}$ ) indicates  $\text{H}_\alpha$  and  $\text{H}_\beta$  protons respectively. The solvents used in recording the UV absorption spectra were UV spectral grade and used as such. Triple distilled water was used for aqueous solutions. The spectra were run in spectra quality solvents using the concentration of  $1 \times 10^{-5}\text{ M}$ . Absorption measurements were made using HITACHI U-2001 recording double beam spectrophotometer.

### Results and discussion

Ultraviolet absorption frequencies of the electronic transition involving the free non-bonding electron and conjugated bonds of DHP have been recorded in ethanol as the solvent in the region 200-600nm. In absorption spectra, transition arises the existence of discrete energy levels in molecules. Some of the transitions are exhibited in the molecules by  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds which form the main system in the present investigation. We know that  $\alpha$ ,  $\beta$ -unsaturated systems exist in *cis* and *trans* forms. These forms are thought to consist of two different independently non-conjugated chromophoric systems namely benzoyl and cinnamoyl groups. Hence, one might expect two independent characteristic bands for the chromophores in chalcones. The study of Szmant and bosso [23], on the absorption spectra of chalcones shows that they exhibit long wavelength band of chalcones 298nm in the hydrocarbon and 312 in alcoholic solution and short wavelength of *cis* chalcones at 225- 200nm. The characteristic of the maximum of the cinnamoyl chromophore lies at 286 nm. Thus, it is evident that the absorption in the  $\alpha$ , $\beta$ -unsaturated carbonyl compounds is due to the transition of the electronic charge as shown in the **Scheme 2** and not due to an isolated system. Although far more attention has been paid to study and interpret the ultraviolet absorption spectra of chalcones, no significant work has been carried out in this direction for chalcones involving DHP system. The present work summarizes the result and conclusion of a detailed research carried out on the ultraviolet absorption spectra of DHP derived from 1,4-benzo dioxo acetophenone. The electronic absorption spectra recorded in alcoholic and non-alcoholic solvents. In all the spectra the principle absorption is only  $\pi \rightarrow \pi^*$  transition occurs. As two peaks around 340 nm and 250 nm, the later transition is less predominant in all the cases. There is no indication of  $n \rightarrow \pi^*$  transition in any of the cases. The prominent absorption maxima ( $\lambda_{\text{max}}$ ) value of chalcone in both alcohol and non-alcohol system are given in **Table 1**.



Scheme 2

**Table 1**  $\lambda_{\max}$  Values of DHP in various solvents

S.NO	solvents	$\lambda_{\max}$ Cm <sup>-1</sup>
1	Methanol	307
2	Ethanol	311.5
3	2-Propanol	318
4	n-butanol	305
5	Carbontetrachloride	313
6	Chloroform	312
7	Dichloromethane	317
8	DMSO	335
9	DMF	334
10	Acetonitrile	320
11	N-Hexane	299.5

### Effects of the solvents on UV spectra

It was thought of interest to study the effect of alcohol on the ultraviolet absorption characteristic of the DHP. It is well known that excited has considerable charge separation relative to its ground state the absorption is shifted to a longer wavelength by increasing the polarity of the solvent. As one of the electronic transitions in the DHP is  $\pi \rightarrow \pi^*$ . This is expected to shift its wavelength of maximal absorption to the longer wavelength increasing the polarity of the solvents. Hence UV spectra of DHP were recorded in n-hexane and ethanol-water mixture of varying dielectric constant. The absorption maximum is considered that due to the electronic transition from a non-solvated ground state to the excited state. The difference in the absorption maxima between those in alcohol-water mixtures and those in hexane is a direct measure of the excited state stabilization energy of DHP under investigation in various alcohol-water mixture  $\lambda_{\max} \{(\text{EtOH-water}) - \lambda_{\max} \text{hexane}\}$  values and dielectric parameters are given in **Table 2**.

**Table 2** F(D) and  $\Delta\lambda_{\max}$  values by varying dielectric constants of alcohol

S.NO	% of ETOH	Dielectric constant(D)	1/D	F(D) = (D-1)/(2D+1)	$\lambda_{\max}$	$\Delta\lambda_{\max}\text{Cm}^{-1}$
1	100	24.30	0.041	0.469	311.5	12
2	90	29.80	0.033	0.475	312	12.5
3	80	35.48	0.028	0.479	313.5	14
4	70	41.07	0.024	0.482	314	14.5
5	60	46.66	0.021	0.484	315	15.5
6	50	52.25	0.018	0.486	317	17.5
n-hexane = 299.5						

The plot of  $\Delta\lambda_{\max}$  versus  $f(D) = D-1/2D+1$  Kirkwood [28] function of dielectric constant as shown **Figure 1** from the perfect linearity between stabilization energy and dielectric constant of EtOH-H<sub>2</sub>O mixtures establishing the fact that the stabilization energy is increased by solvation of excited state. It was thought about great interest to see if any correlation exists between stabilization energy of the excited state and dielectric constant of the medium by varying the alcohol themselves. The solvent effect is best-interpreted in terms of the following properties (a) dielectric behavior (b) the ability of the medium to solvate (c) the ability of protic solvents to form a hydrogen bond with the negative end of the dipole.

Solvatochromism is caused by differential solvation of ground state and excited state of the specially activated molecules. To study the solvatochromism of DHP system, UV spectra recorded in different solvents and the corresponding  $\lambda_{\max}$  value and solvent parameters are given in **Tables 1** and **3**, the investigated chalcone exhibited bathochromic shift as a result of an increase in the solvent polarity. Thus, the solvent plays important role in physical and chemical process and can determine the change in the position of intensity as well as shape of the absorption bands.

Absorption can be influenced by the nonspecific interaction such as dipole-dipole, induced dipole-permanent dipole interaction or by specific interactions such as hydrogen bonding with solvents. The position of absorption bands of DHP in various solvents are correlated with different physical properties [26-31] of the solvent N, D, E, k, H, J, M&N and the corresponding correlation coefficient were deduced given in **Table 4**. The SPSS program was applied, and the mechanism of solvation was discussed the following equation is applied,

$$Y = a_0 + a_1x_1 + a_2x_2 + \dots + a_n X_M$$

where  $y$  is the observed peak location of an absorption band in a given solvent  $a_0$  is regression intercept,  $a_1, a_2, \dots, a_x$  are coefficient which could be determined by the multiple regression analysis techniques using micro statistics SPSS program.  $E = 2.859 \times 10^{-3} / \lambda_{\max}$ .

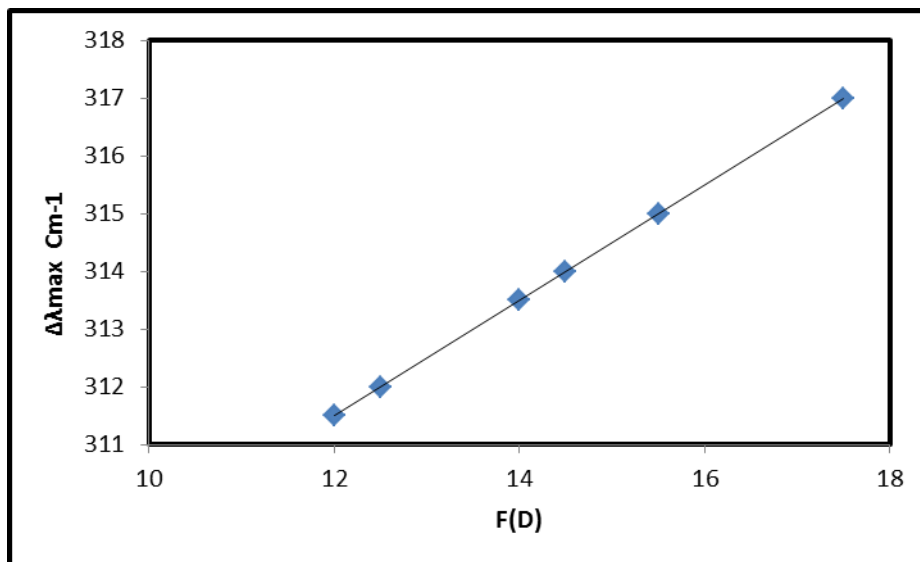


Figure 1 The plot of  $\Delta\lambda_{\max}$  versus  $f(D)$

Table 3 Solvent parameters [24, 25]

S.NO	solvents	(n)	(D)	$E_T^{30}$	AN	$\alpha$	$\beta$	$\pi^*$
1	MeOH	1.3286	32.66	55.4	41.3	0.93	0.62	0.60
2	EtOH	1.3614	24.55	51.9	37.1	0.83	0.77	0.54
3	Prop-2-ol	1.3773	19.92	48.4	33.5	0.76	0.95	0.48
4	But-2-ol	1.3992	17.51	49.7	36.8	0.79	0.88	0.46
5	CCl <sub>4</sub>	1.4603	2.24	32.4	8.6	00	0.10	0.28
6	CHCl <sub>3</sub>	1.4180	4.89	39.1	23.1	0.44	00	0.58
7	CH <sub>2</sub> Cl <sub>2</sub>	1.4451	8.93	40.7	20.4	0.30	00	0.82
8	DMSO	1.4790	46.45	45.1	48.9	00	0.76	1.00
9	DMF	1.4300	36.71	43.2	36.7	00	0.69	0.88
10	CH <sub>3</sub> CN	1.3716	39.94	45.6	37.5	0.19	0.31	0.75

Table 4 Regression coefficients(R) of DHP

S.No	Parameters	Intercept	A1	A2	A3	SD	R
1	K	270.41	99.65	-	-	9.715	0.5500
2	M	242.88	371.73	-	-	9.771	0.5458
3	N	308.13	16.19	-	-	10.280	0.4711
4	E	309.34	0.143	-	-	11.60	0.0990
5	KM	176.34	117.38	439.57	-	6.62	0.8447
6	MN	226.75	410.59	18.400	-	8.00	0.7624
7	KE	265.96	263.21	-1.590	-	6.774	0.8367
8	ME	173.76	556.14	0.7528	-	8.765	0.7055
9	NE	325.50	23.27	-0.4705	-	10.44	0.5351
10	KMN	181.85	101.31	438.96	4.1037	6.998	0.8484
11	KME	210.37	202.93	268.79	-0.8989	6.2321	0.8819
12	KNE	273.53	241.74	5.79	-1.6019	7.089	0.844
13	MNE	205.18	468.99	14.64	0.2707	8.411	0.7716

It is assumed to be an estimate of the peak position for gas spectra Polarity is the most important factor in the solvent parameter which is used for solvatochromic studies. The empirical solvent polarity index  $E_T^{30}$  has been used to study the solvent-solute interaction influence on electronic transition for chalcone. The plot of  $\lambda_{max}$  versus  $E_T^{30}$  is fairly satisfied which denotes the hydrogen bonding plays an important role in the solvatochromism of the DHP. The high value of R is indicating specific interaction in chalcone. The Kirkwood dielectric function K represents the dipolar- dielectric interaction and it is related to the dielectric constants D of the solvent. The functions J and H have been introduced to account for non-specific solute-solvent interactions such as dispersion and dipolar effects. These (J&H) are related to the dielectric constant (D) and the refractive index(n) of the solvents respectively. The function M and N have been introduced to account for the solute permanent dipole solvent induced dipole and solute permanent dipole-solvent permanent dipole interactions respectively. The selected parameters are given in **Table 5**. The multiple correlations coefficient R and the probability of variations  $\rho$  have been considered as a measure of the goodness of fit. The high value of R means the solvent parameter has a good correlation to the spectral shift. The parameters that gave the best correlations in few cases. In this case, the correlation coefficient of DHP with K ME parameters is well satisfied among the others (Table 4). From the presented UV visible spectra, it could be noticed the diversity of the spectra, but it shows appropriate shift which depends on the molecule and solvents used. The largest shift was found in DMSO it shows that bathochromic shift in solvents used is a strong indication  $\pi \rightarrow \pi^*$  the main process that contributes to electronic transition during molecules excitation. The difference in the stabilization of the ground and excited state indicates the intensity of solvent-solute interaction change during the excitation. It also indicates that extended resonance interaction through  $\pi$  electron system of the molecules scheme 2 significantly affects the contribution of the appropriate electronic transitions involved during the excitation.

The difference in stabilization of the ground and excited state of the studied compound was observed as a small bathochromic shift noticed for DHP in DMSO, it is characteristic of molecules of low dipolarity in the ground state, in which a process of the electronic transition is associated with intramolecular charge transfer [26]. This compound contains  $\pi$  electrons delocalization of the aromatic ring with C=O group is operative (a lone pair of carbonyl group). DMSO significantly possess pronounced polar character high value of relative permittivity (46.45) and also high dipole moment (3.96). Higher bathochromic shifts of the investigated compound in the aprotic dipolar solvent DMSO can be explained by the fact that at high at refractive permittivity of the surrounding medium, the energy necessary to bring about charge separation in the excited state is relatively small.

**Table 5** Calculated Solvent parameters based on equation\*[29]

S.NO	Solvents	K	J	H	M	N	FX
1	Methanol	0.4922	0.9134	0.2032	0.1689	0.7102	0.9406
2	Ethanol	0.4896	0.8870	0.2215	0.1813	0.6655	0.9217
3	Prop-2-ol	0.4871	0.9044	0.2302	0.1871	0.0431	0.8920
4	But-2-ol	0.4853	0.8462	0.2420	0.1949	0.6042	0.9044
5	CCl <sub>4</sub>	0.3509	0.2874	0.2740	0.2151	0.0134	0.3827
6	CHCl <sub>3</sub>	0.4466	0.5646	0.2520	0.2013	0.3126	0.6604
7	CH <sub>2</sub> Cl <sub>2</sub>	0.4703	0.7255	0.2606	0.2102	0.4649	0.7986
8	DMSO	0.4946	0.9381	0.2836	0.2209	0.6545	0.9579
9	DMF	0.4931	1.1741	0.2583	0.2053	0.9158	0.9470
10	ACN	0.4937	0.9285	0.2216	0.1814	0.7069	0.9511
11	n-Hex	0.3188	0.2321	0.2289	0.1863	0.0032	0.3120

$$*K = \frac{D-1}{2D-1}; J = \frac{D-1}{D+2}; H = \frac{n^2-1}{n^2+2}; M = \frac{n^2-1}{2n^2+1}; N=J-H; FX = \frac{D-1}{D+1}$$

If the solvent can stabilize the induced dipole in the excited, the electronic transition will require less energy, and due to this absorption bands will be shifted bathochromically the most extensively applied method of values for intermolecular solute/solvent interaction is interpreted by the Linear Solvation Energy Relationship (LSER) [32, 33] concept using the general equation given below.

$$v = v_0 + s\pi^* + a\alpha + b\beta$$

$\alpha$ ,  $\beta$  and  $\pi^*$  are solvatochromic parameters and a, b and s are the solvatochromic coefficients.  $\pi^*$  is an index of the solvent dipolarity/polarizability which is a measure of the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect. 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 the solvent to accept a proton in a solute to solvent hydrogen bond. The correlations of the UV data for DHP were carried out by means of multiple linear regression analysis. It was found that  $\lambda_{\max}$  for DHP in eleven different solvents for which the solvatochromic constants are known showed good correlation with  $\pi^*$ ,  $\alpha$  and  $\beta$  values [33]. The results of the multiple linear regression analysis is

$$\lambda_{\max} = 302.69 + 26.47\pi^* + 8.773\beta - 18.23$$

$$(\pm 1.76) (\pm 2.764) (\pm 2.548) (\pm 2.304)$$

$$R = 0.984, S.E. = 2.336, n = 11$$

The positive signs of the  $s$  and  $b$  indicates a hypsochromic shift with increasing solvent polarity and solvent hydrogen bond acceptor basicity ( $a/s = -0.6887$ ,  $b/s = 0.337$ ). The negative sign of the coefficient indicates a bathochromic shift with increasing solvent hydrogen bond donor acidity. This suggests that most of the solvatochromism in DHP is due to solvent polarity and acidity rather than basicity.

## Conclusion

The solvatochromism of the DHP was analyzed with N, D, E, k, H, J, M&N parameters. The multilinear correlation of the spectral data with solvents properties was established with K, M&E and Kamlet-Taft solvents scales. The solvatochromism in DHP is due to solvent polarity and acidity rather than basicity. In the present investigation, the linear solvation energy relationship has been found to give excellent result when compared to other solvatochromic single parametric equations.

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