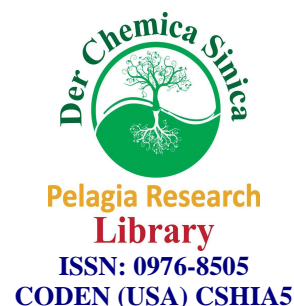




Pelagia Research Library

Der Chemica Sinica, 2013, 4(3):88-92



Effect of substituent and solvent on the electronic spectra of some substituted styryl pyrrolyl ketone

R. Rajalakshmi*, A. N. Palaniappanand and S. Srinivasan

Department of Chemistry, Annamalai University, Annamalaiagar

ABSTRACT

The effects of substituents and solvents have been studied through the absorption spectra of nearly twelve *meta*, *para* and *ortho*-substituted 2-pyrrolyl styryl ketones in the range of 200-400 nm. The effects of substituents on the absorption spectra of compounds under investigation are interpreted by correlation of absorption frequencies with simple and extended Hammett equations. 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.

INTRODUCTION

Chalcones are α , β -unsaturated ketones and they have great existence in the plant Kingdom. It is well known that the most of natural synthetic chalcones are highly biologically active with great pharmaceutical and medicinal applications [1]. Recently they are used as *anti*-AIDS agents [2] cytotoxic with antiangiogenic activity [3, 4] antimalarial [5, 6], anti-inflammatory [7, 8] and antitumor [9, 10]. Although far more attention have been paid to study and interpret the UV absorption spectra of simple chalcones to significant work has been carried out in this direction for chalcones involving 2-pyrrolyl styryl ketone. 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 2-pyrrolyl styryl ketones.

MATERIALS AND METHODS

All the substituted benzaldehyde and 2-acetylpyrrole were purchased from Aldrich Chemical Co. The substituted 2-pyrrolyl styryl ketones were prepared (from) using literature procedure [12]. The solvents used were of spectral grade and are used as such. The purity of the compounds were checked by noting its melting point. Absorption measurements were made using HITACHI UV-2001 recording double beam spectrophotometer.

RESULTS AND DISCUSSION

The UV-absorption spectra have been recorded for twelve *meta*, *para* and *ortho*-substituted 2-pyrrolyl styryl ketones.

In all the absorption spectra the principle absorption is only $\pi^* \leftarrow \pi$ transition and that it occurs as two peaks around 300 nm and 220-250 nm. There is no indication of $\pi^* \leftarrow n$ transition in any of the cases.

The Hammett correlation is made with σ and σ^+ constants in the region of principle maximum of absorption for all the substituted 2-pyrrolyl styryl ketone. The hexane separately and with $\Delta\lambda_{\max}$ values are extremely in significant (Table 1). The poor correlations exhibited above may be due to the system investigated, but may possibly due to the inadequacy of Hammett constants derived from ground state properties of molecules to be used to predict the effect

of substituent in the excited state characteristics of molecule in electronic transition in 2-pyrrolyl styryl ketone and its substituent. It would be rather interesting to drive excited state Hammett constant from the electronic transition studied in the present work.

Table 1. The principal absorption maxima of substituted 2-pyrrolyl styryl ketone

S. No.	Substituent	λ_{\max} (Ethanol)nm	λ_{\max} (Hexane)nm
1.	H	339.80	317.40
2.	<i>m</i> -OCH ₃	342.40	327.60
3.	<i>p</i> -CH ₃	343.00	323.00
4.	<i>m</i> -Cl	341.00	320.20
5.	<i>m</i> -Br	341.40	321.00
6.	<i>o</i> -Cl	340.20	322.00
7.	<i>p</i> -OCH ₃	354.80	336.00
8.	<i>o</i> -OCH ₃	353.60	337.00
9.	<i>m</i> -NO ₂	342.00	327.80
10.	<i>p</i> -Br	342.80	321.40
11.	<i>m</i> -OH	344.40	326.40
12.	<i>p</i> -NO ₂	388.00	331.40

3.1. Effect of solvent

The ultraviolet absorption spectra of the 2-pyrrolyl styryl ketone derived from 2-acetylpyrrole were recorded in hexane and in ethanol-water mixtures of varying dielectric constant. The $\log \Delta\lambda_{\max}$ plotted against ϵ , $1/\epsilon$ and $f(\epsilon) = \epsilon/2\epsilon + 1$ ($\Delta\lambda_{\max} = \lambda_{\max}(\text{ethanol-water}) - \lambda_{\max}(\text{hexane})$). In all the plots there is perfect linearity between the stabilization energy and dielectric constants of the alcohol-water mixtures establishing the fact that the stabilization energy is increased by solvation of the excited state (Figs. 1-3).

In view of above correlation attempt was made to seek similar correlation by varying alcohols themselves. In this case the correlation between $\log \Delta\lambda_{\max}$ and ϵ , $1/\epsilon$ and $f(\epsilon)$ was very poor. But then the failure was compensated by multiple solvent parameters and it is observed that multiple correlation equations predicts very well the properties of alcohols to decide λ_{\max} in poor alcohol (Table 2).

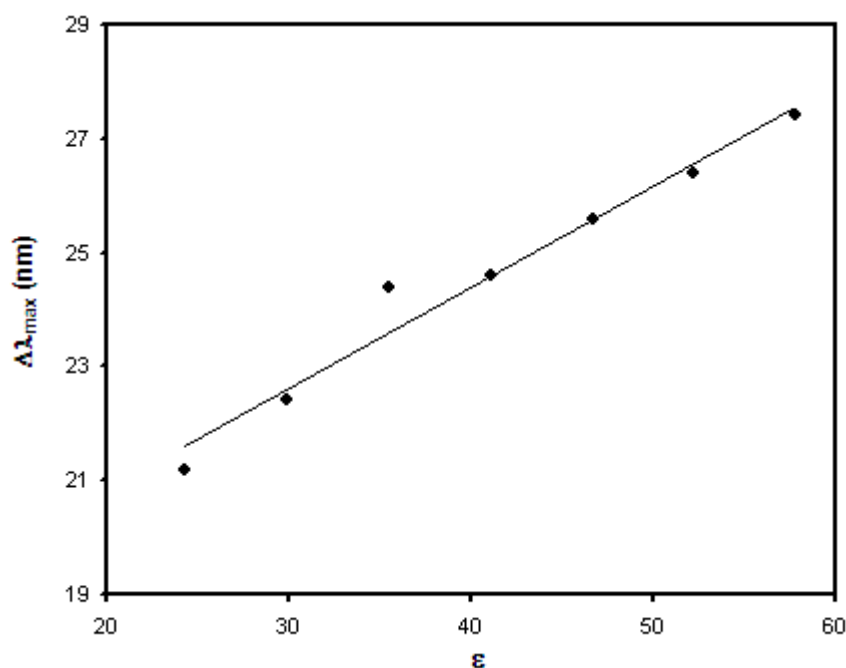
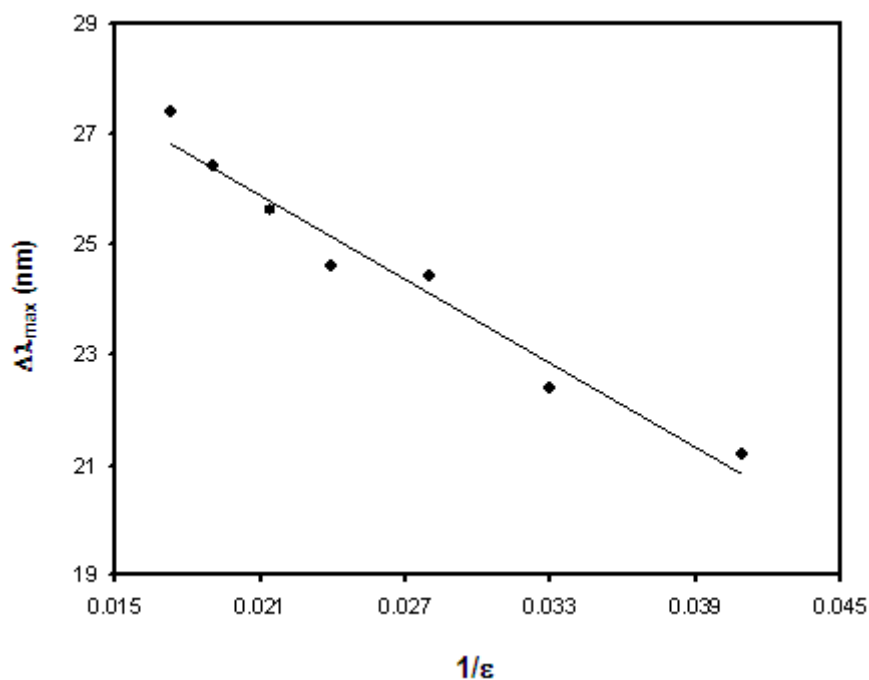
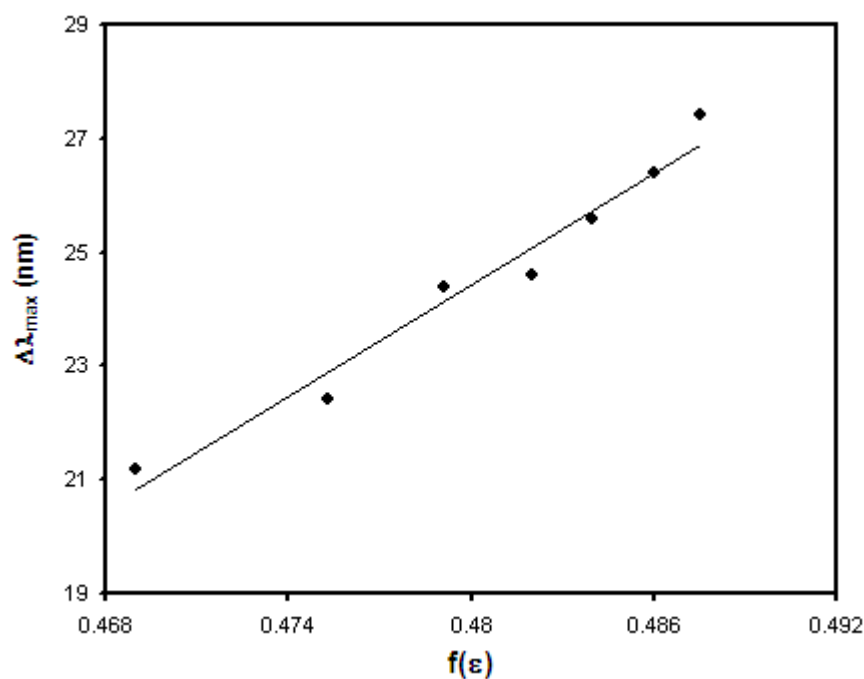


Fig. 1. Plot of $\Delta\lambda_{\max}$ of substituted 2-pyrrolyl styryl ketone versus ϵ

Fig. 2. Plot of $\Delta\lambda_{\max}$ of substituted 2-pyrrolyl styryl ketone versus $1/\epsilon$ Table 2. Correlation equation with σ^* , $f(\epsilon)$, E_s and $n\gamma_H$ constant

S. No.	Correlation	Correlation equation	Solvent
1.	With σ^*	$\log \Delta\lambda_{\max} = 1.3344 + 0.109 \sigma^*$ $r = 0.168, n = 8, SD = 13.980$	1-Butanol, 2-Butanol, 2-Propanol, 2-Methyl-2-propanol, Benzyl alcohol, Methanol, Ethanol, 1-Propanol
2.	With σ^* and $f(\epsilon)$	$\log \Delta\lambda_{\max} = 1.2965 + 0.0294 \sigma^* + 0.1926 f(\epsilon)$ $r = 0.571, n = 8, SD = 0.066$	
3.	With σ^* , E_s and $n\gamma_H$	$\log \Delta\lambda_{\max} = 1.2941 + 0.0501 \sigma^* - 0.04004 E_s + 0.17606 n\gamma_H$ $r = 0.610, n = 8, SD = 0.079$	
4.	With E_s , $f(\epsilon)$ and $n\gamma_H$	$\log \Delta\lambda_{\max} = 1.2955 + 0.03158 E_s + 0.121 n\gamma_H + 0.0238 f(\epsilon)$ $r = 0.548, n = 8, SD = 0.0844$	

Fig. 3. Plot of $\Delta\lambda_{\max}$ of substituted 2-pyrrolyl styryl ketone versus $f(\epsilon)$

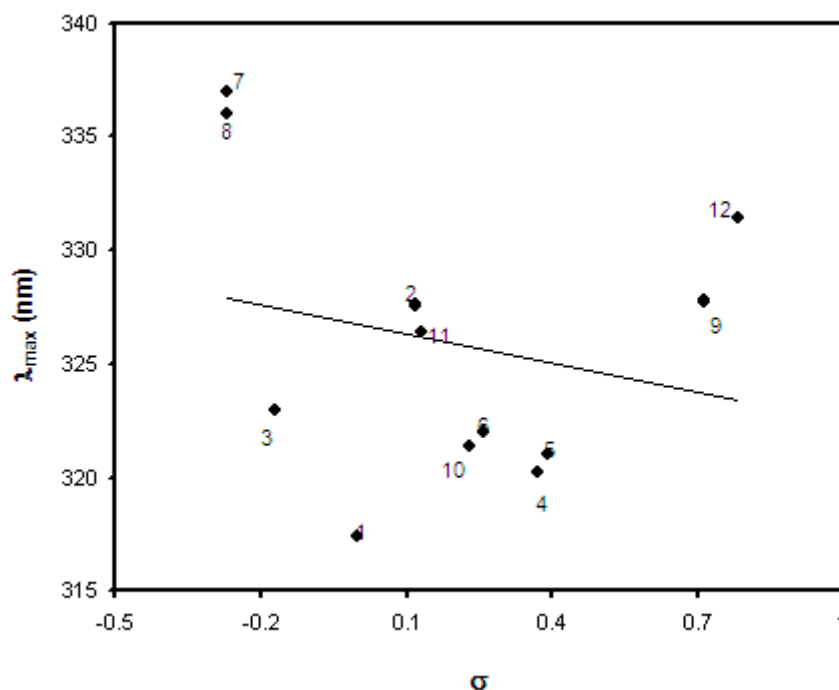


Fig. 4. Plot of λ_{\max} (hexane) of substituted 2-pyrrolyl styryl ketone versus σ

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.*¹¹ which explains the effect of solvent polarity and hydrogen bonding which takes the form

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

Hence α , β and π^* are solvatochromic parameter and a , b and S are solvatochromic co-efficients. The variable α - 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 β 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. π^* 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 2-pyrrolyl styryl ketone for π - π^* transition in seventeen different solvents were carried out using eqn. (2).

$$\begin{aligned} \log \lambda_{\max} &= h + S\pi^* + a\alpha + b\beta \\ &= 2.505 + 0.02431 \pi^* + 0.01184 \alpha + 0.0030 \beta \\ &(\pm 0.00258) (\pm 0.045) (\pm 0.0036) (\pm 0.004) \end{aligned} \quad \dots (2)$$

$$n = 17 \quad R = 0.910 \quad SE = 0.049$$

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 λ_{\max} values for the unsubstituted compound in eighteen different solvents are compared with solvent parameter $E_T(30)$ (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.

Table 3. Absorption maxima for 2-pyrrolyl styryl ketones in polar and non-polar solvents

S. No.	Solvents	λ_{\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

CONCLUSION

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

REFERENCES

- [1] D.N. Dhar, *Chemistry of Chalcones and Related Compounds*; Wiley; N. Y., **1981**.
- [2] J.H. Wu, X.H. Wang, Y.H. Yi, K.H. Lee, *Bioorg. Med. Chem. Lett.* **13** (2003) 1813.
- [3] N.H. Nam, Y. Kim, Y.J. You, D.H. Hong, H.M. Kim, B.Z. Ahn, *Eur. J. Med. Chem.* **38** (2003) 179.
- [4] G. Saydam, H.H. Aydin, F. Sahin, O. Kucukoglu, E. Erciyas, E. Terzioğlu, F. Buyukkececi, S.B. Omay, *Leukemia Res.* **27** (2003) 57.
- [5] X. Wu, P. Wilairat, M.L. Go, *Bioorg. Med. Chem. Lett.* **12** (2002) 2299.
- [6] J.N. Dominguez, J.E. Charris, G. Lobo, N.G. Dominguez, M.M. Moreno, F. Riggione, E. Sanchez, J. Olson, P. Rosenthal, *J. Eur. J. Med. Chem.* **36** (2001) 555.
- [7] T. Tuchinda, T. Santisuk, W.C. Taylor, *Phytochemistry* **59** (2002) 169.
- [8] F. Herencia, M.L. Ferrandiz, A. Ubeda, J.N. Dominguez, J.E. Charris, G.M. Lobo, M.J. Alcaraz, *Bioorg. Med. Chem. Lett.* **8** (1998) 1169.
- [9] Y. Xia, Z.Y. Yang, P. Xia, K.F. Bastow, Y. Nakanishi, K.H. Lee, *Bioorg. Med. Chem. Lett.*, **10** (2000) 699.
- [10] S. Ducki, R. Forrest, J.A. Hadfield, A. Kendall, N.J. Lawrence, A.T. McGown, D. Rennison, *Bioorg. Med. Chem. Lett.* **8** (1998) 1051.
- [11] M.J. Kamlet, J.M. Abboud, M.H. Abraham, R.N. Taft, *J. Org. Chem.* **48** (1983) 2877.
- [12] S.A. Basaif, T.R. Sobahi, A. Khalil, M.A. Hasan, *Bull. Korean Chem.* **26** (2005) 1677.