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Effect of Substituent and Solvent on the Electronic Spectra of Some Substituted N-Pheny Maaleimide

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ABSTRACT

The effects of substituents and solvents have been studied through the absorption spectra of meta,para and ortho-substituted N-Pheny maleimide 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

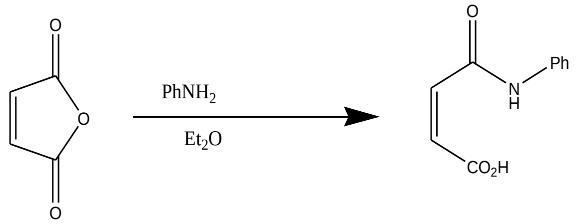
The solvatochromic shift can provide vital information regarding charge distribution in the solute molecule,geometry of the molecule,nature of transition in the ground and excited states [1-5].These effects are predominantly electrostatic and may of induced dipole – induced dipole ,dipole-dipole or hydrogen 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 N- Phenyl Maleamides. 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 N- Phenyl Maleamides.

2. Experimental section

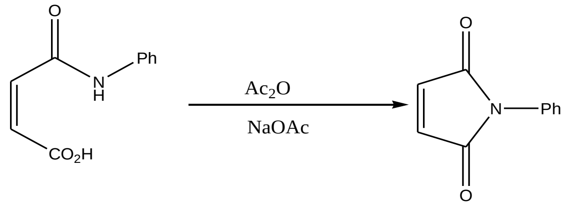
All the reported melting points were taken in open capillaries and are uncorrected (Table.1). In all the cases, the progress of the reaction is monitored by TLC method, which revealed that the reactions were proceeding smoothly in the expected pathway. Mass spectra were recorded on Varian GC/mS# in using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

General procedure for the preparation of N- Phenyl Maleamide

A mixture m *Maleic anhydride and* substituted *aniline* in 200 ml of *ether* was stirred and the resulting thick suspension was stirred at room temperature for 1 hr and then cooled to 15-20° in an ice bath. The product obtained was a fine, cream-colored powder(scheme.1) The maleanilic acid obtained as described above was refluxed with acetic anhydride in presence of sodium acetate and the resulting suspension was dissolved by swirling and heating on a steam bath for 30 minutes. The reaction mixture was then poured into ice water. The precipitated product was filtered, and recrystallized from *cyclohexane.* (scheme2)



(scheme.1)



(scheme.2)

Results and Discussion

The UV-absorption spectra have been recorded for nine *meta*, *para* and *ortho*-substituted N- Phenyl Maleamide In all the absorption spectra the principle absorption is only $\pi^* \leftarrow \pi$ transition and that it occurs as two peaks around300 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 allthe substituted N- Phenyl Maleamide. 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 in adequacy of Hammett constants derived from ground state properties of molecules to be used to predict the effect substituent in the excited state characteristics of molecule in electronic transition in N- Phenyl Maleamide and its substituent. It would be rather interesting to drive excited state Hammett constant from the electronic transition studied in the present work.

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Table 1. The principal absorption maxima of substituted N- Phenyl Maleamide.

S. No.	Substituent	λmax (Ethanol)nm	λmax (Hexane)nm
1	H	281.5	315
2	*m*-CH3	260	275.4
3	*p*-CH3	242.4	266.8
4	*p*-Cl	257	313.4
5	*p*-Br	256.4	269.8
6	*m*-NO2	262.6	341.4
7	*p*-OCH3	243	275.2
8	*p*-COOH	262.6	341.4
9	*p*--NO2	343	280.6

Effect of solvent

The ultraviolet absorption spectra of the N- Phenyl Maleiamide derived from maleic anhydride were recorded in hexane and in ethanol-water mixtures of varying dielectric constant. The log Δλmax plotted against ε, 1/ε and f(ε) =ε/2ε + 1(Δλmax =λmax (ethanol-water) - λmax (hexane)). In all the plots there is perfect linearity between thes tabilization 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).

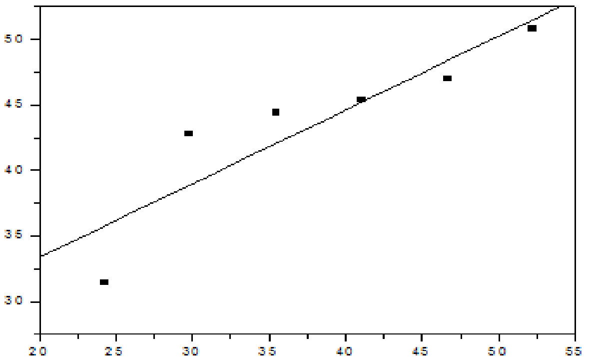

Fig. 1. The plot of λ_{max} of substituted N-phenylmaleimide Vs ∈.

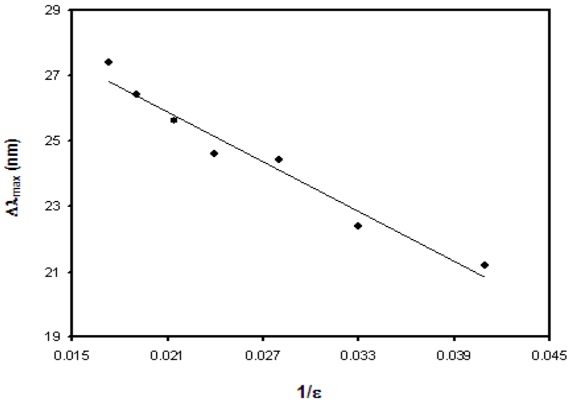

Fig. 2. Plot of Δλmax of substituted N-Phenyl maleimide *versus* 1/ε.

In view of above correlation attempt was made to seek similar correlation by varying alcohols themselves. In this case only a fair correlation was obtained between log Δλmax and ε, 1/ε and f(ε).But then it was compensated by multiple solvent parameters and it is observed that multiple correlation equations predicts very well the properties of alcohols to decide λmax in poor alcohol (Table 2).

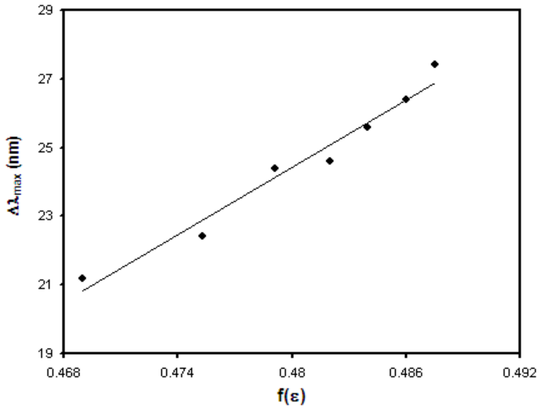

Fig. 3. Plot of Δλmax of substituted N-Phenyl maleimide *versus* f(ε).

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

$\log \lambda_{max} = \gamma_0 + S\pi^* + a\alpha + b\beta$ … (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 asolvent to accept a proton in a solute to solvent hydrogen bond. π* is an index of the solvent dipolarity/polarisabilitywhich 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 N-phenyl maleimide for π-π* transition in eleven different solvents were carried out using eqn. (2).

$\log \lambda^{max} = h + S\pi^* + a\alpha + b\beta$ … (2)

$2.299 + 0.1648\ \pi^* + 0.033\ \alpha + 0.062\ \beta$

n = 11 R = 0.910 SE = 0.024

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'

Table 2. Correlation equation with σ*, f (ε), Es and nγH constant.

S.NO	CORRELATION	CORRELTION EQUATION	SOLVENT
1	With σ*	log Δλmax=0.837+0.927 σ* r = 0.112, n = 8, SD = 0.7955	
2	With σ* and f(ε)	log Δλmax=12.62+4.037 σ* +-24.60 f(ε) r = 0.185, n = 8, SD = 0.861	1-Butanol, 2-Butanol, 2-Propanol, 2-Methyl-2-propanol, Benzyl alcohol, Methanol, Ethanol, 1-Propanol
3	With σ*, Es and nγH	log Δλmax = 3.29+ 0.23 σ*- 4.66Es - 0.344nγH r = 0.693, n = 8, SD = 0.707	
4	With Es, f(ε) and nγH	log Δλmax = 1.07- 0.444 Es+ 208 nγH - .35f(ε) r = 0.701, n = 8, SD = 0.708	

Table 3. Absorption maxima for N-Phenyl maleimide in polar and non-polar solvents.

S.No	SOLVENTS	λmax	logλmax
1	Methanol	301.2	2.47
2	2-Methyl-propan-2-ol	295.4	2.47
3	Propan-1-ol	311.2	2.49
4	Benzyl alcohol	294.6	2.46
5	Butan-1-ol	316.2	2.49
6	Butan-2-ol	315.0	2.49
7	Propan-2-ol	314.2	2.49
8	Ethanol	281.6	2.44
9	Dioxane	313.2	2.49
10	DMSO	284.0	2.45
11	Ethyl acetate	279.2	2.44

indicates a hypochromic shift with increasing solvent hydrogen bond donor acidity.The λ_{max} values for the unsubstituted compound in eighteen different solvents are compared with solvent parameterET (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.

Conclusion

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

References

[1] J.H. Wu, X.H. Wang, Y.H. Yi, K.H. Lee, *Bioor. Med. Chem. Lett. 13* (**2003**) 1813.

[2] N.H. Nam, Y. Kim, Y.J. You, D.H. Hong, H.M. Kim, B.Z. Ahn, *Eur. J. Med. Chem. 38* (**2003**) 179.

[3] G. Saydam, H.H. Aydin, F. Sahin, O. Kucukoglu, E. Erciyas, E. Terzioglu, F. Buyukkececi, S.B. Omay, *Leukenia Res. 27*(**2003**) 57.

[4] X. Wu, P. Wilairat, M.L. Go, *Bioorg. Med. Chem. Lett. 12* (**2002**) 2299.

[5] 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.

[6]S.G.Schulman in“Flurorescenceand phosphorescence Spectroscopy,Physico-chemical Principles and Practice”, Pergmon press New york(1997).

.[7]Y. Xia, Z.Y. Yang, P. Xia, K.F. Bastow, Y. Nakanishi, K.H. Lee, *Bioorg. Med. Chem. Lett., 10* (**2000**) 699.

[8]S.A. Basaif, T.R. Sobahi, A. Khalil, M.A. Hasan, *Bull. Korean Chem. 26* (**2005**) 1677.

[9]G.S.Ulcmumlic and S.D.Petrovic, Ind.J.chem., **41,206 (2002)**

[10].R.Rajalakshmi.et al., *Der Chemica Sinica**, 2013, 4(3):88-92***

[11] T. Tuchinda, T. Santisuk, W.C. Taylor, *Phytochemistry 59* (**2002**) 169.

[12] M.J. Kamlet, J.M. Abboud, M.H. Abraham, R.N. Taft, *J. Org. Chem. 48* (**1983**) 2877.