

CORRELATION OF ELECTRONIC SPECTRAL DATA OF 2-PHENYL-1, 8-NAPHTHYRIDINIC ACID IN APROTIC SOLVENTS

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Abstract

The effect of the aprotic solvents on the electronic transition $\pi \rightarrow \pi^*$ for 1, 8-naphthyridinic acid in eight aprotic solvents have been studied. Good correlation with the solvatochromic equations and the electronic transition $\pi \rightarrow \pi^*$ has been noticed.

Key word: Naphthyridinic acid, $\pi \rightarrow \pi^*$ transition, aprotic solvents, solvatochromic equation

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Introduction

Solvent effects on $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ electronic spectral transitions are well described by the solvatochromic equation

$$xyz = xyz_0 + s(\pi^* + \delta) + a\alpha + b\beta \dots\dots\dots [1]$$

This has been successfully applied to correlate medium effects of many types of properties, including position of maximal absorption in UV, visible absorption and fluorescence spectra¹⁻³. The π^* -scale of dipolarity –polarizabilities describe the ability of a solvent to stabilize a solute charge or dipole by virtue of its dielectric effect; the α -scale of hydrogen bond donor (HBD) acidities, measure by solvent ability to share a proton in a solvent to solute hydrogen bond; the β -scale of hydrogen bond acceptor (HBA) basicities, measure the solvent ability to share a proton from an hydrogen bond donor solute, δ is a polarizability correction term equal to (0.0) for non-chlorinated aliphatic solvents, (0.5) for polychlorinated aliphatic, and (1.0) for aromatic solvents; s, d, a and b represent the response of xyz to the solvents polarity- polarizability and hydrogen bonding properties. The xyz term in equation (1) may be the logarithm of rate constant, equilibrium constant, the position or intensity of maximal absorption in an UV and other spectra.

Correlations of these types were the subject of extensive study, which has been so far reported³⁻⁷. In order to investigate the solvent effects on $\pi \rightarrow \pi^*$ electronic spectral transition, we thought it might be of interest if we examine the effect exerted by the presence of a second nitrogen atom on the electronic absorption spectra.

Experimental

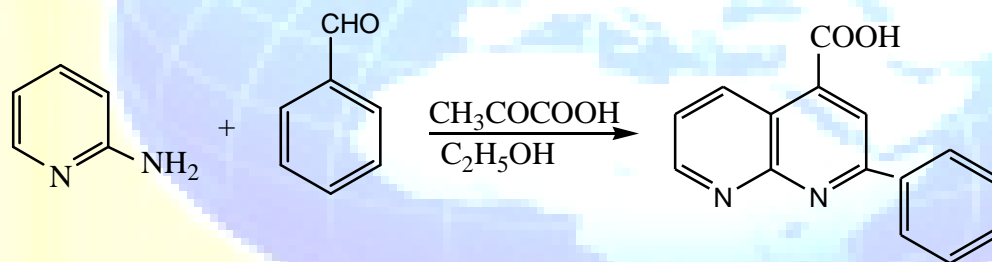
Melting points were determined on a Stuart melting point apparatus and are uncorrected. The solvents used in the spectroscopic measurements were of spectroscopic grade whenever possible, commercial solvents were purified by standard method⁸. The solvents used were listed in table 1. All UV spectral measurements were carried out at about 20°C. ($5 \times 10^{-5}M$) concentration of the corresponding compound was prepared. The UV spectral measurements were performed on a Pye-Unicam Sp-800 double beam UV-visible spectrophotometer. The analysis of results and solvatochromic equation carried out by HYUNDAI computer.

Procedure for preparation of 2-phenyl-1, 8-naphthyridinic acid

Benzaldehyde (0.025 mol) was placed in around bottomed flask fitted with reflux condenser protected with CaCl_2 tube. Absolute ethanol (10 mL) was added and the mixture was heated in a water bath for 10 minutes, 2-aminopyridine (0.025 mol) in absolute ethanol (5mL) was added in one portion followed by drop wise addition of pyruvic acid (0.025 mol) with vigorous stirring and maintaining the temperature at $40\text{-}50^\circ\text{C}$, the addition lasts one hour. The reaction mixture then refluxed in water bath for further 6 hours, and then left to stand overnight. The solvent was removed under vacuum and the oily residue was treated with water to give solid material with after crystallization from ethanol gave a pale yellow crystals. The purity of the product was checked by TLC and its melting point, the IR and ^1H NMR spectra was in agreement with the literature value⁹ (153°C) mp $152\text{-}153^\circ\text{C}$, 66% yield

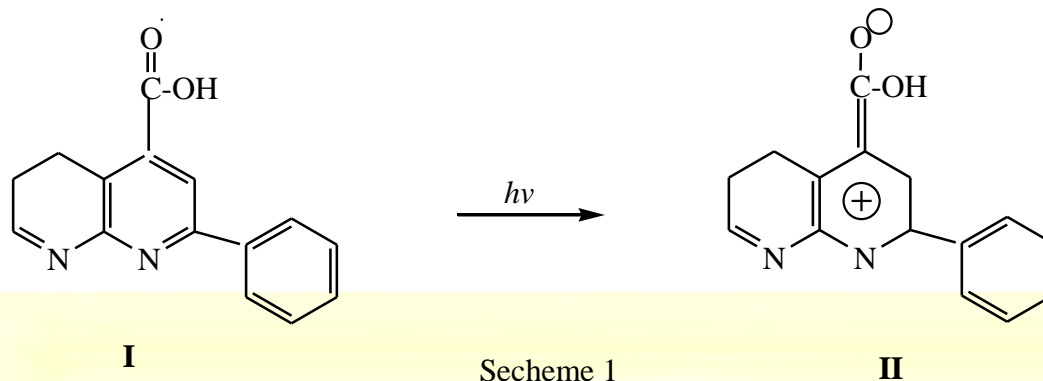
Results and Discussion

2-Phenyl-1, 8-naphthyridinic acid was obtained according to the following scheme



The results obtained in this work are similar to a previously reported work¹⁰⁻¹² which have been carried out on cinchophen derivatives. The UV spectra were measured of 1, 8-naphthyridinic acid in eight solvents, the region of absorption could be attributed to $\pi \rightarrow \pi^*$ transition. It was found that solvatochromic shifts were toward the red with increasing solvent polarity (negative s value) eq. 2,3,4, which suggest that UV absorption spectral bands showed bathochromic shift with increasing solvent polarity and follow the π^* pattern of behavior. The data are listed in table 1 together with the solvent parameters.

Electronic spectral transitions from a ground state (I) to an excited state (II) are given in scheme 1. The charge is generated in the electronic excited state and the structures are stabilized by solvent polarity in accord with simple electrostatic theory. Hence the polar solvent facilitates excitation and result in a bathochromic shift as compared to the non-polar solvents.



A linear plot is obtained by using solvatochromic equation by the method of multiple parameter least square correlation (multiple linear regression analysis), where (ν), the wave number is plotted against (π^*) polarity-polarizability term. A straight line is obtained of correlation coefficient (0.960) and intercepts (40.064×10^{-3}) and slope (-9.641×10^{-3}) equation 2.

$$(10^3 \text{ cm}^{-1}) \nu_{\text{max}} = 40.064 - 9.641 (\pi^* + 0.834 \delta) \pm 0.698 \text{ ----- [2]}$$

$$n = 8 \quad r = 0.96$$

Then the same procedure was followed by introducing β in multi-regression analysis, such introduction improve the correlation coefficient (equation 3).

$$(10^3 \text{ cm}^{-1}) \nu_{\text{max}} = 40.195 - 9.139 (\pi^* + 0.834 \delta) \pm 0.660 - 1.641 \beta \pm 0.738 \text{ ----- [3]}$$

$$n = 8 \quad r = 0.97$$

While no effects of correlation coefficient when α is introduced, equation 4.

$$(10^3 \text{ cm}^{-1}) \nu_{\text{max}} = 40.173 - 8.936 (\pi^* + 0.834 \delta) \pm 0.74 - 1.815 \beta \pm 0.798 - 1.178 \alpha \pm 1.781 \text{ ----- [4]}$$

$$n = 8 \quad r = 0.96$$

Figure (1) shows plot of ν_{max} (obs.) vs ν_{max} (calc.) according to equation 4, d-value in equation 2 is 0.834 calculated using standard equation reported previously¹. The positive sign of d means that the polarity correction term reinforce the π^* dipolarity – polarizability effect of the solvent. Negative sign of (s), equations 2, 3, 4 indicate the inverse proportion between polarity – polarizability term of the solvent and wave number (ν), i.e. direct proportion with λ (bathochromic shift) means greater stabilization of the excited state (II) through the solvent to a larger extent than the ground state (I), hence reduce energy required in the excitation of π electrons.

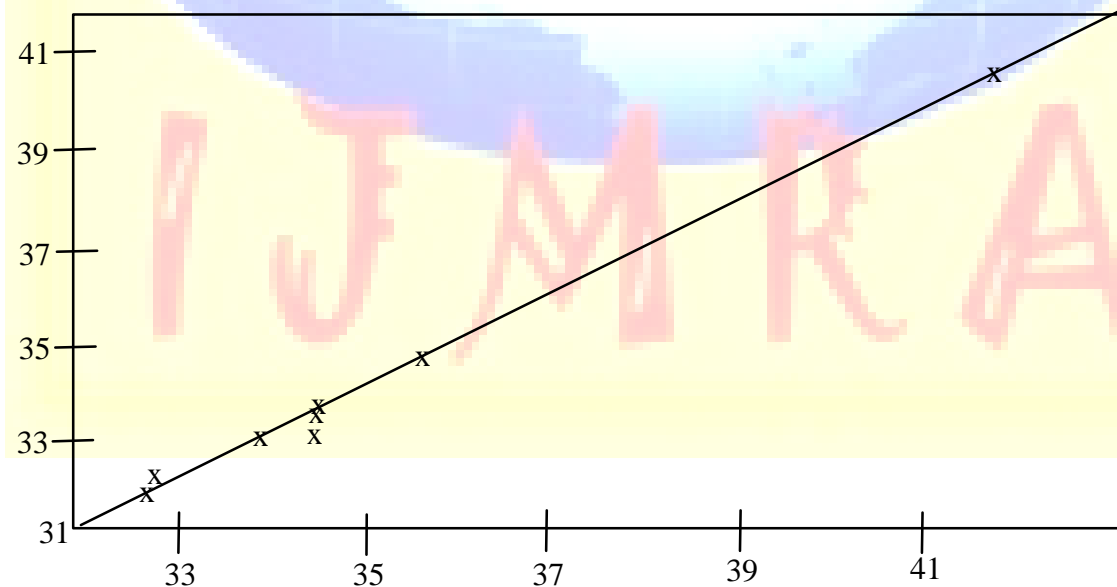
Negative sign of a and b means inverse proportion of acidity and basicity term and ν , (direct proportion with λ) i.e. the solvent stabilize the excited state (II).

On the light of the results obtained it is reasonable to conclude that solvatochromic equation is quite suited to correlate solvents effects parameters for this compound.

Table1: $\pi \rightarrow \pi^*$ Electronic spectral data of 2-phenyl-1, 8-naphthyridinic acid in various solvents and solvent parameters used for multiple linear correlation

No.	Solvent	$\nu_{\max} 10^3 \text{ cm}^{-1}$	π^*	β	α
1	n-Hexane	41.66	- 0.08	0.0	0.0
2	Bezene	34.48	0.59	0.1	0.0
3	Toluene	33.89	0.54	0.11	0.0
4	Chloroform	32.78	0.76	0.0	0.38
5	Dioxane	34.48	0.55	0.37	0.0
6	Ethyl acetate	34.48	0.55	0.45	0.0
7	Diethyl ether	35.71	0.29	0.47	0.0
8	Acetone	32.78	0.71	0.37	0.0

ν_{\max} . Observed X 10^3 cm^{-1}



ν_{\max} . Predicted X 10^3 cm^{-1}

Fig.* (1): Plot of ν_{\max} observed VS ν_{\max} predicted according to equation 4

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