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Spectroscopic Studies: Aprotic Solvent Effect on Electronic Absorption Spectra of Biologically Active Compound Derived from 1, 8- Naphthyridine

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Abstract

The effect of the aprotic solvents on the electronic transition $\pi \rightarrow \pi^*$ for compound (in seventeen aprotic solvents have been studied. Good correlation with the solvatochronic equation and the electronic transition $\pi \rightarrow \pi^*$ has been noticed. This result was compared with our studies on similar compounds derived from other nucleus such as quinoline. In 1,8-naphthyridine derivative, the naphthyridine residue showed no noticeable changes in the solvatochromic equation than the previous studies.

Key words: Aprotic solvents, electronic transition, solvatochromic effect, naphthyridine derivative

Introduction

Solvents as a medium for chemical and physical processes have always played a very important role in chemistry. Solvent effects on *n* $\rightarrow \pi$ and $\pi \rightarrow \pi^*$ electronic spectral transition are well described [1,2] by solvatochromic equation of general formula:

$$xyz = xyz + s(\pi^* + ds) + a\alpha + b\beta \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

Where π scale of dipolarity- polarizablites describes the ability of a solvent to stabilize solvent change or dipole by virtue of its dielectric effect; the α – scale of hydrogen bond donor (HBD). Acidities measure the solvent ability to share a proton, while basicities measure the solvent ability to share a proton from a 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 terms in equation (1) may be the logarithm of rate constant, equilibrium constant and the position or intensity of maximal absorption in UV and other spectra.

Solvatochromic equations have been successfully applied to correlate medium effects of many types properties, including position of maximal absorption in UV, Visible absorption and Fluorescence spectra. Correlations of these types of absorption were the subject of extensive study [3, 4]

In continuing our previous work [5] concerning the solvent effects on $\pi \rightarrow \pi^*$ electronic spectral transition, we thought it might be of interest if we continue examining the effect excreted by the presence of other fused pyridine ring containing halogen substituent in the naphthyridine system rather than the quinoline residue. Therefore we prepared compound (I) according to the procedure described by Ayoub et al [6]. Since naphthyridine or naphthyridone derivatives are of great importance because

the 1, 8-naphthyridine skeleton is present in many compounds that have been isolated from natural sources, and have various biological activities [7], among these Gemifloxacin which is an antimicrobial and have naphthyridine skeleton. It is well known that many substituted 1,8-naphthyridine derivatives were used as local anesthetic [8].Recently quinolines and 1,8- naphthyridine have been exploited in cancer chemotherapy [9[

Many methods have been proposed to prepare various types of 1,8-naphthridine system [10-11] involves the reaction of 2-aminopyridine derivatives with carbonyl compound containing active methylene group or with β- keto ester [12] or condensation of ethanolic 2- amino-3- formyl pyridine in the presence of piperidine with active methylene containing compounds, aldehydes, acyclic and cyclic ketones or diketones [13-15]. The Vilsmeier-Haack reagent used in this preparation has been proved to be a versatile reagent capable of execution a large variety synthetic transformation.

The aim of this work was to synthesize new 1, 8- naphthyridine derivatives and examine the effect exerted by the presence of halogen and aldehyde group on the electronic absorption spectra of the synthesized compound.

Experimental

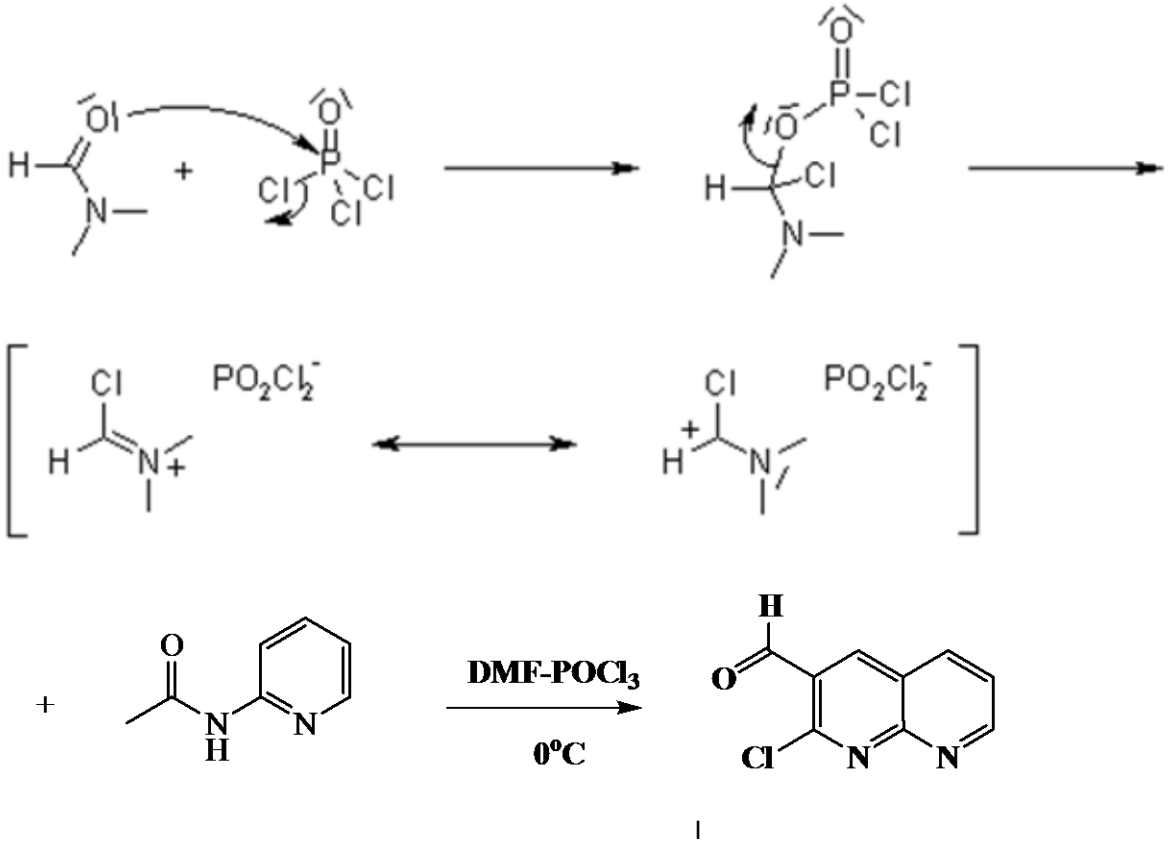
Melting points were determined on a Stuart melting points apparatus and are uncorrected. The solvents used in the spectroscopic measurements were of spectroscopic grade whenever possible commercial solvents were purified by standard method [16], the solvents used were listed in table (1).

All UV spectral measurements were carried out at about 20 ^{o}C, and were performed on Pye-Unicam Sp-800 double beam UV-Visible spectrophotometer. The concentration of the corresponding compound was (5 x 10^{-5} M), the analysis of results and solvatochromic equation carried out by HYUNDAI computer.

Synthesis of 2- chloro-3-formyl -1, 8 –naphthyridine (I)

To a solution of N-(pyridine -2-yl) acetamide (5 mmoles) in dry DMF (15 ml) at 0 ^{o}C, phosphorus oxy chloride (60 mmoles) was added drop wise with continuous stirring, the reaction mixture was kept at (85-90 ^{o}C) with stirring overnight, after that the reaction mixture was poured into crushed ice, stirred for 30 min and the resulting solid filtered, washed well with water and dried, recrystallization from ethanol gives pure product (I).Yield (60%) pale yellow colour, mp 158-160 ^{o} C.The purity of the product waschecked by TLC and by both IR and ^{1}HNMR spectroscopy. The scheme of the reaction is outlined

below.



I

Reaction scheme 1

This compound also showed a very bright intense colour which change in solvents as well as in acidic and basic media. The behaviors in the UV spectra in seventeen aprotic solvents were measured. The region of absorption could be attributed to $\pi \rightarrow \pi^*$ it was found that solvatochromic shifts solvent polarity (negative s value) equation 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 the table below, together with solvent parameters. Electronic spectral transition from a ground state I to an excited state II is given in scheme 2. The charge generated in the electronic excited state and the structures are stabilized by solvent polarity is 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 (υ) the wave number is plotted against (π^*) polarity-polarizablite term. A straight line is obtained of correlation coefficient (0.960) and intercepts (40.064 $x10^{-3}$) and slope (-9.641$x10^{-3}$) equation 2.

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

n= 8 r = 0.96

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

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

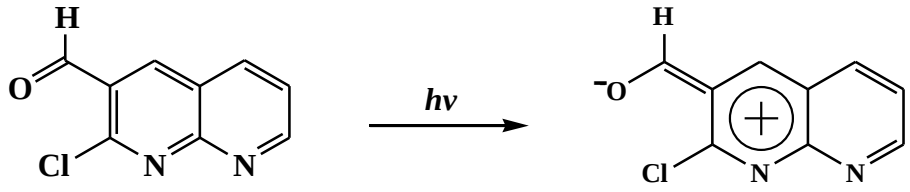
n=8 r=0.97

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

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

n=8 r=0.96

Figure (1) shows plot of υ_{max} (obs.) vs, υ_{max} (calc.) according to equation 4, d –value in equation 2 is 0.834 calculated using standard equations reported previously. The positive sign of (d) means that the polarity correction term reinforces the dipolarity-polarizability effect of the solvent. On the other hand, negative sign of (s) , equation 2,3,4 indicated the inverse proportion between dipolarity –polarizability term of the solvent and wave number (υ), i.e. direct proportion with λ (bathochromic shift) means greater stabilization of the excited state (II) though the solvent to larger extent than the ground 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 terms and υ, (direct proportion with λ) i.e. the solvent stabilize the excited state (II).



I II

Scheme 2

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

Table1: $\pi \rightarrow \pi^*$ Electronic spectral data of 2-chloro-3-formyl-1, 8-naphthyridine in various solvents and solvent parameter used for multiple linear correlation

No.	Solvent	υ_{max} 10^3 cm^{-1}	π^*	β	A
1	n.hexane	41.66	0.08	0	0.0
2	Cyclohexane	40.82		0	0.0
3	Benzene	34.48	0.59	0.1	0.0
4	Toluene	33.89	0.54	0.11	0.0
5	Chlorobenzene	33.89	0.71	0.07	0.0
6	Bromobenzene	33.89	0.79	0.06	0.0
7	Carbontetra chloride	37.03	0.29	0	0.0
8	Chloroform	32.78	0.76	0	0.38
9	Trichloroethylene	35.25	0.53	0	0.0
10	Dioxane	34.48	0.55	0.37	0.0
11	Ethyl acetate	34.48	0.55	0.45	0.0
12	Diethyle ether	35.71	0.29	0.47	0.0
13	Tetrahydrofuran	33.89	0.58	0.55	0.0
14	Telrahydropyran	33.08	0.51	0..54	0.0
15	Acetone	32.78	0.71	0.37	0.0
16	Acetonitrile	32.78	0.76	0.31	0.0
17	Dimethylformanide	31.74	0.88	0.69	0.0

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