Scientific paper

Concentration and Temperature Effects on the Electronic Absorption Spectra of 1-pyridinyl-2-methylene-benzenecarbohydrazonic Acid Following Solvatochromic Studies

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Abstract

In this work, UV–Vis. electronic spectra of 1-pyridinyl-2-methylene-benzene carbohydrazonic acid (**L**) have been studied. The different bands observed have been assigned to the proper electronic transitions. The solvatochromic behavior of this compound is investigated by studying their electronic spectra in organic solvents with different polarities. The longer wavelength band is assigned to an intermolecular charge transfer (CT) transition. The solvated H-bonding complexes formed between dimethylformamide and **L** is also investigated. ΔG, and K_f values of this complex have been determined. Effects of temperature increase and concentration changes on the longer spectroscopic wavelength band of 1-pyridinyl-2-methylene-benzenecarbohydrazonic acid were studied too.

Keywords: Solvatochromic, Hydrogen bonding, Solute-solvent interactions

1. Introduction

Solvatochromism is the pronounced change in the position and sometimes intensity of an electronic absorption or emission band of a compound in solution when the polarity of the medium is changed. A bathochromic (or red) shift of the absorption band with increasing solvent polarity is known as positive solvatochromism and hypsochromic (or blue) shift is expressed as negative solvatochromism.

Solvatochromic compounds exhibit large differences between the dipole moments of their ground and excited states. In general, two groups of compounds show this behavior. The first group is organic molecules where an electron-donating group is linked by a conjugated system to an electron-accepting fragment. Organometallic complexes composed of central metal and organic ligands with a π-electron system are the second important family.[1]

Significant solvent-dependent spectral variations may also arise from self-aggregation of dyes in solution. The monomer may be solvatochromic, and it may not be easy to distinguish the contribution of self-aggregation to the observed solvatochromism, especially in media where the dye is poorly soluble.[1,2]

Because of their sensitivities to environmental changes, wide applications for solvatochromic compounds have been found in the study of solute-solvent interactions, mainly in the characterization of bulk or microenvironments. Solvatochromic dyes also are used to establish empirical scales of solvent polarities.[3] Since these empirical scales may be used to characterize any solvent or solvent mixture, solvatochromism plays an important role in study of a wide variety of solvent-dependent processes.[1,3]

In this work, effect of 11 different solvents including tetrahydrofuran (THF), toluene, carbone tetrachloride (CCl_4), dichloromethane (CH_2Cl_2), chloroform ($CHCl_3$), acetonitrile (CH_3CN), 1-buthanol, ethanol (EtOH), methanol (MeOH), dimethyl sulfoxide (DMSO) and dimethyl formamide (DMF), on UV–Vis. spectra of 1-pyridinyl-2-methylene-benzene carbohydrazonic acid (**L**) have been studied (Figure 1).

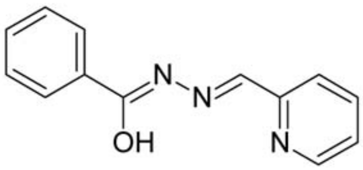

Figure 1. Chemical structure of 1-pyridinyl-2-methylene-benzene-carbohydrazonic acid (**L**).

L is a hydrazone which is a kind of asymmetric Schiff's base. Schiff's bases (also called azomethines or imines) are functional groups with the general formula of $R_1R_2C=N-R_3$. Schiff's base can be divided into two groups; symmetric and asymmetric Schiff's base. Hydrazones are the members of the asymmetric Schiff's bases. Hydrazones are a class of organic compounds with the general structure of $R_2C=NNR_2$ which are related to ketones and aldehydes by the replacement of the oxygen with NNR_2 functional group. These compounds are commonly formed through the reaction of hydrazine on ketones or aldehydes.[4,5]

2. Results and Discussion

2. 1. Solvatochromic Study

UV–Vis. electronic spectra of 1-pyridinyl-2-methylene-benzenecarbohydrazonic acid (**L**) in eleven organic solvents with different polarities were studied. UV-Vis. absorption spectra of **L** was measured in THF, toluene, CCl_4, CH_2Cl_2, $CHCl_3$, CH_3CN, 1-buthanol, EtOH, MeOH, DMSO and DMF. Figure 2 shows absorption spectra of a 1.65×10^{-5} mol L^{-1} of **L** in these solvents. As it can be seen from Figure 2, in the most solvents tested the main band of compound **L**, located in the spectral range of 265–330 nm. According to this figure, change in polarity of the organic solvents does not affect the solvation of **L**. However, in some solvents including DMF, MeOH, THF, and DMSO, **L** shows another band in the spectral range of 350–430 nm. Absorption maxima (λ_{max}) and molar absorption coefficients (L mol^{-1} cm^{-1}) of compound **L,** in various solvents are summarized in Table 1.

Table 1. Absorption maxima (λ_{max}) and molar absorption coefficients of 1-pyridinyl-2-methylene-benzenecarbohydrazonic acid in various eleven organic solvents.

Solvent	λ_{max} (nm)	molar absorption coefficient
THF	300	21171
	391	1229
Toluene	300	25086
CCl_4	298	22771
CH_2Cl_2	299	22343
$CHCl_3$	302	23171
CH_3CN	303	24886
1-Buthanol	305	21343
EtOH	305	21086
MeOH	303	22029
	385	2114
DMSO	305	23257
	390	1314
DMF	300	11457
	376	21829

Shorter wavelength band in UV region observed for **L** in different solvent system is assigned to $\pi \rightarrow \pi^*$ transition of the benzenoid system towards the other ring (pyridinyl group) which is characterized by a high electron accepting character present in its structure. As it can be seen, the main band of compound **L**, located in the spectral range of 265–330 nm, exhibits an apparent shift towards longer wavelengths in different solvents according to the sequence: $CCl_4 < CH_2Cl_2 <$ Toluene ~ THF ~ DMF $< CHCl_3 < CH_3CN <$ MeOH < 1-Buthanol ~ EtOH < DMSO. This shift does not completely agree with the polarity change of the organic solvents and, therefore, it can be considered as a result of combination of several solvent characteristics such as basicity, polarity and H-bond-accepting ability. Furthermore, the electronic spectra of compound **L** in DMF comprise a new band appearing at much longer wavelength, as shown in Fig. 2 curve 11. This behavior can presumably be due to the fact that the solute molecules are liable to form a solvated complex with DMF molecules through an intermolecular H-bonding.[7–9] Since the charge-transfer forces play an important role in H-bonding, this

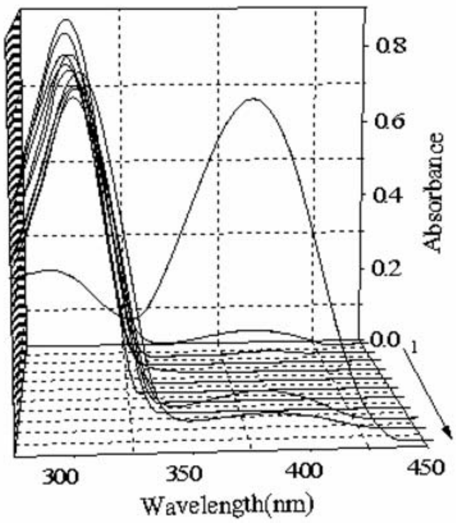

Figure 2. The electronic absorption spectra of a 1.65×10^{-5} mol L^{-1} of 1-pyridinyl-2-methylene-benzenecarbohydrazonic acid (**L**) in different solvents: (1) THF (2) Toluene (3) CCl_4 (4) CH_2Cl_2 (5) $CHCl_3$ (6) CH_3CN (7) 1-Buthanol (8) EtOH (9) MeOH (10) DMSO (11) DMF.

additional band is a result of an intermolecular charge transfer (CT) transition. This phenomenon is due to an electron transfer from the lone pair of electrons at oxygen atom of DMF molecule to the antibonding orbital of OH bond of the phenolic moiety (compound, **L**). The appearance of this band in DMF as a solvent can be attributed to its high basicity as well as its pronounced character as a strong proton acceptor.

2. 2. Concentration Effect

Effect of the concentration on the electronic absorption spectra of **L** is shown in Figure 3. The corresponding absorbance–concentration plots are shown in Figure 4. While the absorbance of 300 nm band increases linearly with concentration of **L** from 4.45×10^{-7} to 4.75×10^{-5} mol L^{-1} with R^2 of 0.99, the corresponding plot at 377 nm shows a nonlinear behavior. It is interesting to note that the observed straight line at 300 nm is in confirmation of the assignment of this band to an intramolecular electronic transition.[7–9] On plotting the absorbance of new band appearing at longer wavelengths against the molar concentration of **L** from 4.45×10^{-7} to 4.75×10^{-5} mol L^{-1}, a nonlinear relationship was obtained, which can be considered as an evidence for the intermolecular CT nature of this band.

Good convincing evidence for the intermolecular CT nature of second band is attained from the non-linear relationship between the absorbance of this band and the molar concentration of this compound.

Further support is achieved by studying the spectroscopic behavior of this compound in DMF containing increasing amounts of ethanol, $CC1_4$, $CHCl_3$ or CH_3CN. It is evident that with increasing DMF concentration, the absorbance of the intramolecular CT band decreases, whereas a new band appears at a longer wavelength (Figure 5).

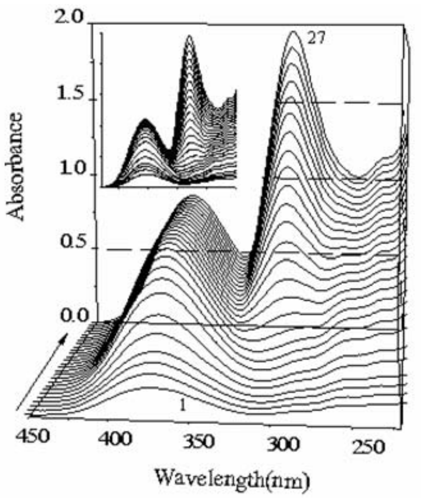

Figure 3. Effect of the concentration on the electronic absorption spectra of **L** in DMF; Curves 1–27 represent: 4.45; 16.0; 25.9; 38.0; 50.10; 67.0; 88.9; 106.8; 124.6; 142.4; 160.2; 177.9; 195.8; 213.6; 231.4; 249.2; 267.0; 284.8; 302.6; 320.4; 338.2; 362.1; 380.9; 404.1; 427.0; 449.0; 474.9×10^{-7} mol L^{-1} solutions, respectively. The inset shows the corresponding plot for more details in two dimensions. The arrows show the directions of absorbance changes by increasing the concentration of **L.**

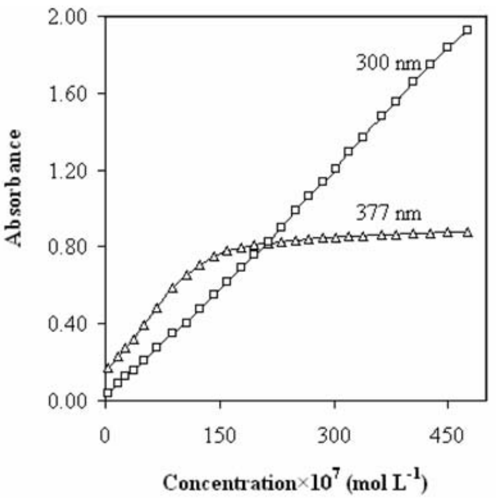

Figure 4. Plot of absorption *vs.* concentration for **L** in DMF at room temperature at the position of the two absorption maxima according to Figure 3.

The observed behavior in different solvent mixtures indicated that DMF molecules have a greater tendency to form solvated complexes with the solute molecules than other tested solvents. This is due to the low ionization potential of DMF as well as its high H-bond accepting character.

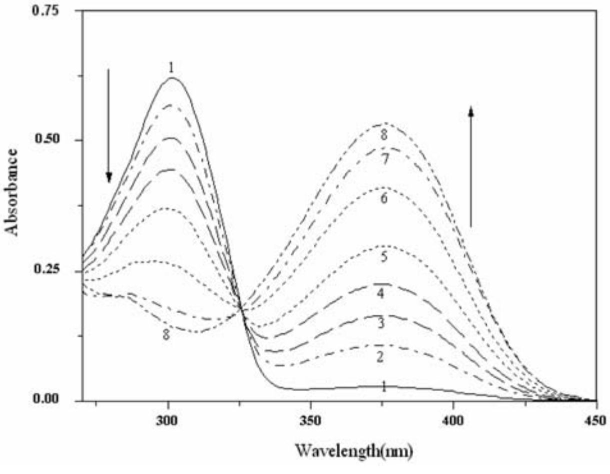

Figure 5. The electronic absorption spectra of 8.0×10^{-6} mol L^{-1} of **L** in DMF-CCl_4 mixtures: (1) 0.50 M DMF; (2) 2.25 M DMF; (3) 3.83 M DMF; (4) 5.00 M DMF; (5) 7.11 M DMF; (6) 8.86 M DMF; (7) 10.35 M DMF; (8) 13 M DMF. The arrows show the directions of absorbance changes with increasing DMF concentration.

2. 3. Temperature Effect

An interesting behavior is obtained by studying the effect of temperature on the low energy band of compound **L** in DMF as solvent.[7,8,10] Spectra of compound **L** in DMF at different temperatures are shown in Figure 6. As it can be seen, raising the solution temperature from 20 °C to 65 °C resulted in significant decrease in the band intensity. Based on the above results, it can be concluded that an increase in temperature of a 3.0 × 10^{-6} mol L^{-1} solution of **L** in DMF increases the molecule energy, charge delocalization and weakens the intermolecular hydrogen bonding, and consequently assists the solute–solvent dissociation. This can be considered as further evidence that this band corresponds to an association process through solute–solvent interactions.

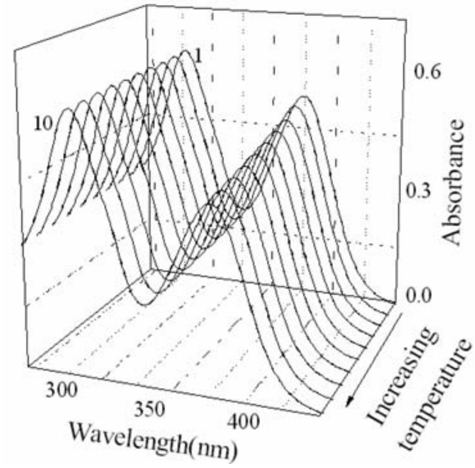

Figure 6. Effect of temperature increase on the electronic absorption spectra of 3.0 × 10^{-6} mol L^{-1} solution of **L**, in DMF; Curves 1–10: 20; 25; 30; 35; 40; 45; 50; 55; 60; 65 °C.

2. 4. Thermodynamic Parameters of Solvation

The formation constants, K_f, of different solvated molecular complexes of compound **L** with DMF were determined from the variation of the absorbance at a given wavelength of their intermolecular CT band with increasing DMF concentration. The equation used is as follow:[9,11]

$$\log C_{DMF} = \log K_f + \log\left(\frac{A - A_0}{A_1 - A}\right) \qquad (1)$$

where A_0 and A_1 are absorbances of the compound **L** in the low dielectric constant solvent and DMF, as a high dielectric constant solvent, and A is the absorbance in the mixed solvent. A plot of $\log C_{DMF}$ *vs.* $\log(A-A_0/A_1-A)$ gives a straight line. From the intercept of this line K_f can be evaluated.

Gibbs free energy (ΔG) of the solvated complexes can be obtained from equation (2):

$$\Delta G = -RT \ln K_f \qquad (2)$$

K_f values and **ΔG** for the hydrogen bonding solvated complexes of **L** in different solvent mixtures are given in Table 2. As it is obvious from Table 2, the resulting K_f and ΔG values in different mixed solvents decrease in the order of DMF–CCl_4 > DMF–$CHCl_3$ > DMF–EtOH > DMF–CH_3CN. It is clearly observed that this sequence is very sensitive to the difference in the dielectric constants of binary mixture components, i.e., K_f and ΔG values decrease with increasing dielectric constant of the solvent mixed with DMF.[7,9]

Table 2. K_f values and **ΔG** for the hydrogen bonding solvated complexes of 1-pyridinyl-2-methylene-benzenecarbohydrazonic acid (**L**).

System	$\mathbf{K_f}$	**ΔG (kJ mol^{-1})**
DMF-CCL$_4$	85.25	–2.61
DMF-$CHCl_3$	76.05	–2.46
DMF-EtOH	69.36	–2.40
DMF-CH_3CN	53.63	–1.25

3. Conclusions

1-pyridinyl-2-methylene-benzene carbohydrazonic acid (**L**) displayed one band in the spectral range of 280–330 nm in various organic solvents. This band attributed to π → π* transition in benzenoid system involving the entire electronic system of the compound. L also showed another band in longer wavelength in DMF solution. The longer wavelength band displayed is assigned to an intermolecular charge transfer (CT) transition. The effects of temperature increase and concentration dependent spectroscopic changes on the longer wavelength band of **L** confirm the intermolecular CT transition. The observation of a special behavior for compound **L** in the presence of DMF indicates that DMF has a greater tendency to form a solvated complex with the solute molecules. This is because of the low ionization potential and high hydrogen bond accepting character of DMF. ΔG and K_f values for the resulting complexes have been also reported.

4. Experimental Section

Schiff's base **L**, with the chemical name of 1-pyridinyl-2-methylene benzene carbohydrazonic acid, was synthesized and purified using a previously reported method.[6] The organic solvents used (THF, toluene, CCl_4, CH_2Cl_2, $CHCl_3$, CH_3CN, 1-buthanol, EtOH, MeOH, DMSO and DMF) were all of analytical grade from Merck or BDH companies. Other chemicals were reagent grade or better and obtained from Fluka or Merck.

Stock solutions (10^{-3} mol dm^{-3}) of the compound **L,** were prepared by dissolving an accurately weighed amount of the target compound in the required amount of the appropriate solvents. Solutions of lower concentrations, used in the spectral measurements, were obtained by appropriate dilutions of the stock solution.

A Shimadzu (Japan) model 1650PC double-beam spectrophotometer was used for recording the electronic absorption spectra.

5. References

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Povzetek

Proučevali smo elektronski spekter 1-piridinil-2-metilen-benzen karbohidrazonijeve kisline v različnih topilih v UV-Vis območju. Opazili smo razliko v vrhovih elektronskih spektrov, ki jo lahko pripišemo posameznim elektronskim prehodom. Vrhovi, ki se pojavijo pri večjih valovnih dolžinah, so tako posledica intermolekularnega prenosa naboja. Raziskovali smo tudi komplekse, ki nastanejo s tvorbo vodikovih vezi med dimetilforamidom in 1-piridinil-2-metilen-benzen karbohidrazonijevo kislino ter določili ravnotežno konstanto, K_f, ter Gibbsovo prosto energijo, ΔG, za tvorbo tega kompleksa.