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The Effects of Solvent and pH on the Electronic Spectral Properties of Indolino Spirobenzoxazine

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Authors' contributions

This work was carried out in collaboration between both authors. Author VNM designed the study and wrote the protocol. Authors VNM and IVM preformed the statistical analysis, managed the literature search and wrote the first draft of the manuscript. Both authors read and approved the final manuscript.

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ABSTRACT

The UV-visible spectra of indolino spirobenzoxazine were recorded in polar protic solvents, methanol and ethanol and polar aprotic solvent, acetone. The results showed a hypsochromic shift in the wavelength of maximum absorption with increase in solvent polarity. pH variation from 3-11 showed significant effects on the absorption properties of the compound. The electronic spectral properties have been shown to correlate successfully with solvatochromic parameters using two variables linear solvation energy relationship (LSER) at 95% confidence level. The contribution of the solvatochromic parameters to the solute-solvent interaction has also been evaluated. Hydrogen bond donor acidity showed 63-67% contribution to the solute-solvent interaction whereas dipolarity/polarizability and hydrogen bond acceptor basicity contributed 37% and 33% respectively.

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Keywords: Spirobenzoxazine; solvatochromic parameter; electronic spectra; solvent effect; pH influence.

1. INTRODUCTION

Indolino spirobenzoxazine represents one of the most important series of photochromic compounds of spirooxazines. They exhibit both normal and reversed photochromism [1]. The photochromic reaction of this compound is the reversible heterolytic cleavage and rebinding of the pyranyl Cspiro-O bond, yielding a coloured open and colourless closed form respectively. Indolino spirobenzoxazine comprises of two heterocyclic nearly planar moieties, indoline and benzoxazine, linked by a tetrahedral spiro-carbon that insulates the two π–electron systems from conjugation [2]. The two halves are orthogonal and the absorption spectrum of the spirooxazine consists of localized transitions arising from a particular half of the molecule without interaction with the other half. The electronic absorption spectra of the closed form of the spirooxazines consist of localized π-π* transitions in the UV region. The absorption bands of these spirooxazines strongly depend on the solvent used. Absorption spectra measured in solvents with different polarity, show modifications in intensities, positions and shapes of the absorption bands [3].

The solvent effect on electronic spectra known as solvatochromism, is exhibited as changes in absorption band frequencies governed by the physical properties of the solvent such as refractive index, dielectric constant, polar and non-polar nature, etc. and is independent of the chemical nature of the solvent. These changes are a result of physical intermolecular solute-solvent interaction forces (such as ion-dipole, dipole-dipole, dipole-induced dipole, hydrogen bonding), which tend to alter the energy difference between the ground state and excited state of the absorbing species containing the chromophore. Solvatochromism of the open form of spirooxazines has been given much attention. This may be due to application of the photochromic properties of the compound in molecular switches and optical devices. Negative solvatochromism - in which the wavelength of maximum absorption, λ_{max} value decreased with an increase in the solvent polarity, and positive solvatochromism - in which the λ_{max} value increased with an increase in the solvent polarity, have been reported [4].

The specific and non-specific solute-solvent interactions are estimated from the wavelength (absorption maximum) using an empirical parameter of solvents polarity called $E_T(30)$ [5]. $E_T(30)$ values are based on negative solvatochromic pyridinium-N-phenolate betaine dye which exhibits one of the largest solvatochromic effects ever observed. The $E_T(30)$ value for a solvent is defined as the transition energy measured in kilocalories per mole (kcal/mol) [6] and can be determined according to Eq. (1).

$$E_T(30) = 28591.5/\lambda_{max}\,(\text{nm}) \qquad (1)$$

Where λ_{max} is the longest wavelength of π→π* absorption band of betaine dye.

Although $E_T(30)$ values have been used to interpret solute-solvent interaction [7], the most successful treatment involves the use of normalized $E_T(30)$ values represented as E_T^N [8]. E_T^N values are dimensionless and can be determined according to Eq. (2).

$$E_T^N = [E_T(\text{solvent}) - 30.7] / 32.4 \qquad (2)$$

Quantitative assessment of solvents effects on electronic spectra has been made using Kamlet-Taft equation, given by Eq. (3) [9].

$$\bar{\nu} = \bar{\nu}_0 + s\pi^* + b\beta + a\alpha \qquad (3)$$

Where π* is an index of solvent dipolarity / polarizability which measures the ability of the solvent to stabilize a charge or a dipole by virtue of its dielectric effect, α is a measure of the solvent hydrogen bond donor (HBD) acidity, β is a measure of the solvent hydrogen bond acceptor (HBA) basicity, $\bar{\nu}_0$ is the regression value of the solute property in the reference solvent cyclohexane and $\bar{\nu}$ is the solute property such as wavenumber of maximum absorption in the UV/visible spectrum. The regression coefficients s, b and a in Eq. (3) measure the relative susceptibilities of the solvent-dependent solute property (absorption frequency) to the indicated solvent parameters.

Spectral measurement depends on the localization of protons. Chemical structures that are prone to influence by varying the hydrogen ion concentration (pH) of the medium also show modification of their electronic properties. The positions and intensities of π-π* band exhibit a marked sensitivity to pH changes because of changes in the interaction of non-bonding electrons with the π-system.

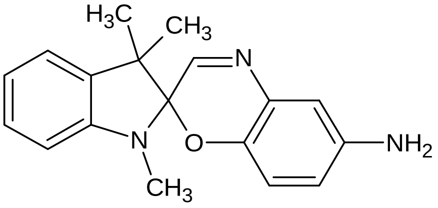
In this paper, we investigate the effects of solvents and pH on the electronic spectral properties of indolino spirobenzoxazine using polar protic and polar aprotic solvents, and also correlate the spectral properties with solvatochromic parameters to evaluate the contributions from HBD, HBA and dipolarity / polarizability to the solute-solvent interaction.

2. MATERIALS AND METHODS

Indolino spirobenzoxazine (ISBO) was obtained from our previous work [10]. The solvents used were spectroscopic grade (Merck). UV-visible spectra were recorded on Sunny UV-7804AC UV-visible spectrophotometer at 27ºC. The indolino spirobenzoxazine was dissolved in the solvents (methanol, ethanol and acetone) to give a concentration of 5.0×10^{-3} mol/L. The absorption spectra of 3 mL aliquot were taken between 200-800 nm wavelengths on the UV-visible spectrophotometer with cell path length of 1 cm. The effect of pH was investigated in ethanol in the pH range 3-11. The pH adjustment was monitored with the help of a pH meter until the desired pH was attained using 0.1 M HCl and 0.1 M NaOH for acid and alkaline range, respectively. Multiple regression analysis was performed using IBM SPSS Statistics version 21.

3. RESULTS AND DISCUSSION

The structure of indolino spirobenzoxazine (ISBO) is shown (1).



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Scheme 1. Structure of Indolino spirobenzoxazine

The Uv-visible absorption spectra of indolino spirobenzoxazine were recorded using two polar protic solvents, methanol and ethanol, and one polar aprotic solvent, acetone. The values of the absorption maxima in the different solvents are shown in Table 1. Three absorption bands were observed for ISBO in all the solvents. They include: absorption maxima in the range 249-300 nm (peak 1) due to π→π* transition; absorption maxima in the range 405-418 nm (peak 2) which may be attributed to n→π* transition; absorption maxima at 543 nm (peak 3) due to π→π* transition [11].

Table 1. Absorption maxima of indolino spirobenzoxazine in organic solvents

Solvent	Absorption maxima λ_{max} (nm)		
	Peak 1	Peak 2	Peak 3
Methanol	249	418	543
Ethanol	295	414	543
Acetone	300	405	543

3.1 Effect of Solvent

It is obvious that the absorption maxima of ISBO are affected by the type of solvent used as shown by Fig. 1. There is a hypsochromic shift in the absorption maxima of the first absorption band (peak 1) as the polarity of the solvent increases. This may be due to better stabilization of the molecule in the ground state relative to the Franck-Condon excited state with increasing solvent polarity. A shift of 5 nm was observed from acetone to ethanol, and 45 nm from ethanol to methanol. A slight bathochromic shift was also observed for peak 2 ($\Delta\lambda_{max}$ = 13 nm) as the solvent polarity increases from acetone to methanol. The band at 543 nm (peak 3) was not influenced by the solvent. Bands that are insensitive to solvents interactions are due to local transitions [12].

3.2 Effect of pH

It is interesting to see how pH variation affects the absorption properties of indolino spirobenzoxazine. Three absorption bands were also observed (Fig. 2). Peak 1 did not show significant changes in λ_{max} with changes in pH. Rather, significant changes were exhibited by peaks 2 and 3. A particular and interesting feature is the spectra recorded for pH of 9, where peaks 2 and 3 merge to form a plateau within the range 467-586 nm, and pH of 11 where peak 3 diminishes to form a shoulder at 488-490 nm. Such changes may be consistent with changes in the molecular skeleton due to reorganization of conjugation of the molecule.

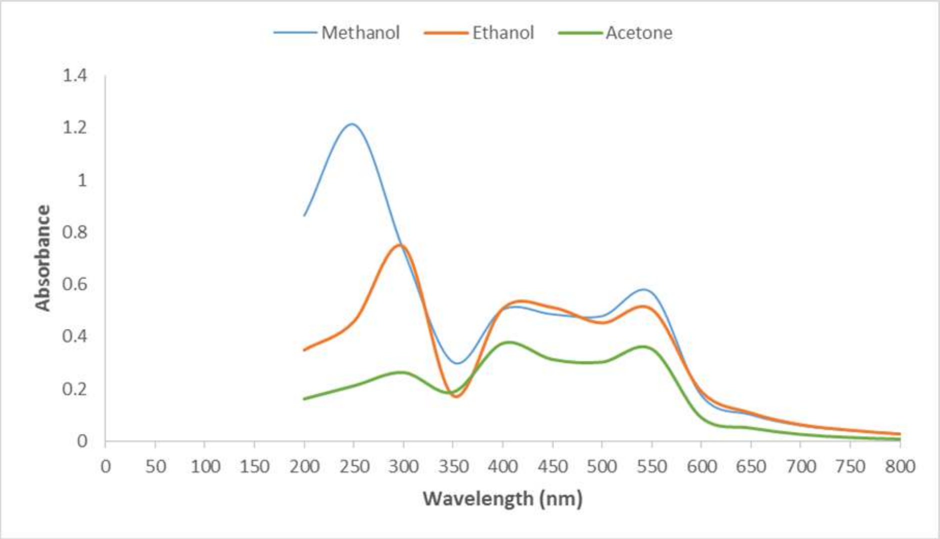

Fig. 1. UV-visible spectra of indolino spirobenzoxazine in different solvents

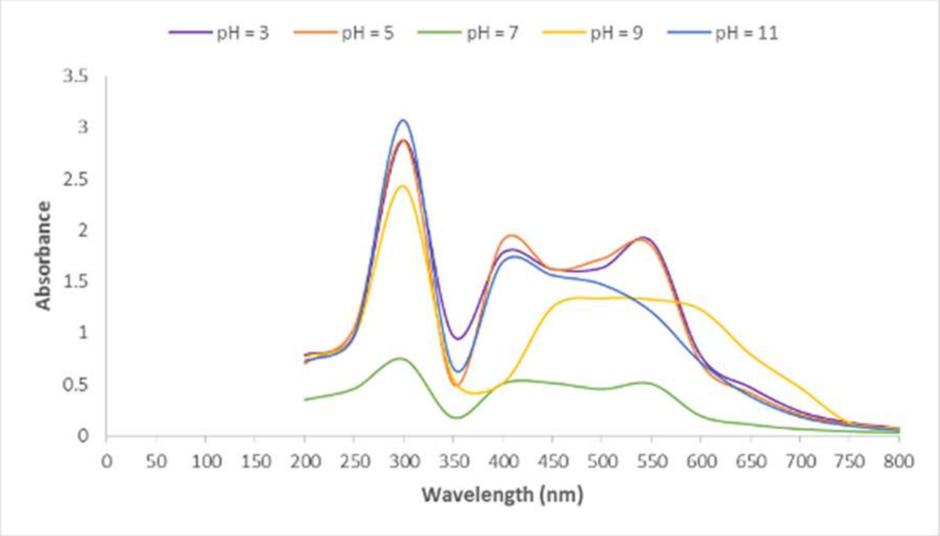

Fig. 2. UV-visible spectra of indolino spirobenzoxazine in ethanol at different pH

3.3 Correlation of Solvent Parameters

To quantitatively assess the solvatochromic behavior of indolino spirobenzoxazine, spectroscopic properties were correlated with relevant solvent polarity parameters, α, β and π*. For this purpose, the absorption data were converted to corresponding transition energies, E_T(ISBO) using Eq. (1) and the data are given in Table 2. To bring the solvent parameters to the same scale, E_T(ISBO) values were normalized to E_T^N (ISBO) using Eq. (2), and the normalized values are also presented in Table 2.

A single parameter regression model for the evaluation of solute-solvent interaction was first employed. The solvents parameters were subjected to regression analysis using LSER (Eq. 4).

$$E_T^N(\text{ISBO}) = E_{T\,0}^N + aX_1 \quad (4)$$

Where $E_{T\ 0}^N$ is the regression constant. The regression coefficient, a, measures the sensitivity of the solvent parameter (X_1) toward the solute property, E_T^N. The different solvent parameters (X_1) used for the regression analysis were obtained from literature [13] and are given in Table 3. Although successful correlation of E_T^N values with solvent parameters have been reported in literature [14-15], it was observed that none of the solvent parameters showed any statistically significant correlation with the absorption properties of peaks 1 and 2 using the single parameter regression model at 95% confidence level.

A two-parameter regression model was then tested using Eq. (5). The absorption properties (peaks 1 and 2) showed successful correlation with solvent parameters with this model. The correlation was statistically significant at 95% confidence level for all the solvent parameters. The correlation statistics are presented in Tables 4 and 5.

$$E_T^N(\text{ISBO}) = E_{T0}^N + aX_1 + bX_2 \qquad (5)$$

The multiple correlation coefficient (R) indicates that E_T^N of ISBO can be predicted with high accuracy. The coefficient of determination (R^2) given as 1 shows that 100% of the investigated absorption properties can be explained by the solvent parameters and the model is a best fit for the correlation.

Since the model gave the same R^2 value for all the solvent parameters tested, the best model was chosen based on least residual. Residual is the difference (variance) between the experimental value and that predicted by the model and the one with the least value was taken as the best model. The best model for peak 1 was given by dipolarity/polarizability (π*) and hydrogen bond donor (α) acidity corresponding to least residual (Eq. 6) whereas for peak 2, the best model was given by hydrogen bond donor (α) acidity and hydrogen bond acceptor (β) basicity (Eq. 7). This may explain the reason peak 1 was more influenced by solvent polarity because of greater contribution from dipolarity / polarizability, exhibiting hypsochromic shift as the solvent polarity increases whereas pH variation in the same solvent (ethanol) showed insignificant influence on peak 1, but, more influence was displayed on peak 2 due to contribution from hydrogen bond donor (acidity (α) and hydrogen bond acceptor (β) basicity.

$$\text{Best model (peak 1): } E_T^N(\text{ISBO}) = -2.303 + 3.621\alpha + 2.091\pi^* \qquad (6)$$

$$\text{Best model (peak 2): } E_T^N(\text{ISBO}) = 1.50 - 0.262\alpha - 0.127\beta \qquad (7)$$

The contribution of the solvatochromic parameters to the solute-solvent interaction was evaluated using the best model. For peak 1 (best described by α and π*), hydrogen bond donor acidity contributed 63% whereas dipolarity / polarizability contributed 37% to the solute-solvent interaction. For peak 2 (best described by α and β), contribution from hydrogen bond donor acidity was 67% while hydrogen bond acceptor basicity contributed 33%.

Table 2. Observed E_T and E_T^N of indolino spirobenzoxazine in organic solvents

Solvent	$E_T(30)$	E_T^N	E_T(ISBO) in kcal/mole			E_T^N(ISBO)		
			Peak 1	Peak 2	Peak 3	Peak 1	Peak 2	Peak 3
Methanol	55.40	0.76	114.83	68.40	52.65	2.60	1.16	0.68
Ethanol	51.90	0.65	96.92	69.06	52.65	2.04	1.18	0.68
Acetone	42.20	0.35	95.30	70.60	52.65	1.99	1.23	0.68

$E_T(30)$: transition energy of reference dye; E_T^N: normalized $E_T(30)$

Table 3. Solvent parameters used for regression

Solvent	α	β	π*
Methanol	0.98	0.66	0.60
Ethanol	0.86	0.75	0.54
Acetone	0.80	0.48	0.62

Table 4. Regression fits to solvatochromic parameters with two parameters model (peak 1)

Solvent parameters		R	R^2	Regression coefficients			Residual#
X_1	X_2			E_{T0}^{N}	a	b	
α	β	1.00	1.00	-0.95	4.12	-0.73	-8.90E^{-16}, -4.40E^{-16}, -4.40E^{-16}
α	π*	1.00	1.00	-2.30	3.62	2.09	-4.40E^{-16}, 0, -4.40E^{-16}
β	π*	1.00	1.00	-11.28	5.31	17.30	2.20E^{-15}, 0, 1.50E^{-15}

 # Residual between experimental and predicted absorption data

Table 5. Regression fits to solvatochromic parameters with two parameters model (peak 2)

Solvent parameters		R	R^2	Regression coefficients			Residual#
X_1	X_2			E_{T0}^{N}	a	b	
α	β	1.00	1.00	1.50	-0.26	-0.13	0, 0, 0
α	π*	1.00	1.00	1.28	-0.35	0.36	2.20E^{-16}, 0, 2.20E^{-16}
β	π*	1.00	1.00	2.16	-0.511	-1.10	-2.20E^{-16}, 0, 0

#Residual between experimental and predicted absorption data

4. CONCLUSION

Electronic absorption properties of indolino spirobenzoxazine are dependent on solvent polarity. A hypsochromic shift in the wavelength of absorption maxima was exhibited as the solvent polarity increases. The absorption properties in the range, 405-418 nm (peak 2) showed significant influence with pH variation. The spectral properties also showed satisfactorily correlation with solvatochromic parameters, α, β and π* using linear solvation energy relation (LSER). The spectral properties of the indolino spirobenzoxazine was influenced by dipolarity / polarizability, hydrogen bond donor acidity and hydrogen bond acceptor basicity.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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