

## SYNTHESIS AND SOLVATOCHROMIC BEHAVIOUR OF SOME HETEROCYCLIC ISONICOTINOHYDRAZIDE SCHIFF BASES

*Tolulope M. Fasina, Cordelia U. Dueke-Eze, Oluwole B. Familoni*

*Department of Chemistry, University of Lagos, Akoka, Lagos State.*

### Abstract

The solvatochromic behaviour of three heterocyclic Schiff bases derived from isonicotinic acid hydrazide (INH) and pyrrole-2-carboxaldehyde (**L1**), furan-2-carboxaldehyde (**L2**) and thiophene-2-carboxaldehyde (**L3**) was studied in nine solvents of different polarities. The electronic transition properties were investigated using the Kamlet-Taft parameters, dielectric function, refractive index function and Catalan parameters. The results indicate that the hydrogen bond acceptor properties of the solvent are more effective in directing the solvatochromic behavior of the Schiff bases

\* Corresponding author:

[tfasina@unilag.edu.ng](mailto:tfasina@unilag.edu.ng)

Received 19 April 2017,

Revised 25 May 2018,

Accepted 26 May 2018

**Keywords:** Solvatochromism, Schiff bases, Electronic absorption spectra, Kamlet-Taft parameters, Catalan Parameters.

## 1. Introduction

Schiff bases particularly those containing nitrogen, oxygen and sulphur as donor atoms have been reported to show antibacterial, antiviral, antifungal and antituberculosis activities [1-5]. In addition, these compounds exhibit interesting photophysical properties and are also used in the design of various molecular electronic devices due to their photochromic behavior [6-7]. The spectral behaviour of organic compounds is used in structure elucidation, as it provides information on their ground state and excited state structures. The nature of solvent used in such study is crucial to an understanding of the solute-solvent interactions existing in solutions under investigation. Thus, a study of the solvatochromic behaviour of molecules is therefore important in understanding the photophysical and other related properties of a compound [8-9]. Several empirical parameters of solvent polarity have been developed to interpret solute-solvent interaction using spectroscopic data. In this study, we employed the Kamlet-Taft parameters (dielectric function  $f(\epsilon) = (\epsilon - 1)/(\epsilon - 2)$ , refractive index function  $f(n) = (n^2 - 1)/(n^2 - 2)$ , hydrogen bond acceptor capacity ( $\alpha$ ), and hydrogen bond donor capacity ( $\beta$ )) and Catalan parameters (solvent polarity/polarizability (SPP), acidity of solvents (SA) and basicity of solvents (SB)) in the investigation of the solvatochromic behaviour of three heterocyclic INH Schiff bases.

## 2. Experimental

All chemicals and solvents were obtained commercially from Aldrich Chemicals Co Ltd, Germany and used without further purification. Melting points were determined on a Stuart SMP3 melting point apparatus and are uncorrected. Infrared spectra were recorded in the region 4000-400  $\text{cm}^{-1}$  on a FTS 7000 series Digilab Win-IR Pro spectrometer equipped with the ATR (attenuated total reflectance) Diamond Selenium accessory. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Varian 300 MHz spectrometer using deuterated chloroform ( $\text{CDCl}_3$ ) as solvent with tetramethylsilane (TMS) as the internal reference. Elemental analyses were performed with a Perkin-Elmer 2400 CHNS/O analyzer. The electronic spectra of the compounds were recorded in solutions made using spectroscopic grade solvents namely acetonitrile, 1-butanol, 1,4-dioxane, ethanol, ethyl acetate, methanol, 1-propanol, dimethylsulphoxide (DMSO) and *N,N*-dimethylformamide (DMF) on a Cecil Super Aquarius 9000 series UV-Vis spectrophotometer using 1 cm quartz cell at room temperature immediately after preparing the solutions.

### *Typical Synthesis of the Schiff Bases*

Equimolar quantities (0.10 mmol) of isonicotinic acid hydrazide (INH) and the corresponding aldehyde (pyrrole-2-carboxaldehyde (**L1**), furan-2-carboxaldehyde (**L2**) or thiophene-2-carboxaldehyde (**L3**)) and were dissolved in hot absolute ethanol (10 ml) with the addition of 0.3 ml glacial acetic acid. The mixture was heated under reflux at 65 °C for 4 h. The precipitate obtained was separated by filtration, re-crystallized from ethanol and dried in a desiccator.

## 3. Results and discussion.

### *Synthesis*

The Schiff bases **L1** - **L3** were obtained in moderate yields from the condensation of INH with the heterocyclic aldehydes namely pyrrole-2-carboxaldehyde (**L1**), furan-2-carboxaldehyde (**L2**) and thiophene-2-carboxaldehyde (**L3**) (Scheme 1). The compounds were purified by recrystallization from ethanol.

### Scheme 1: Synthetic route to Schiff bases L1-L3

The formation of the compounds was confirmed by the presence of a band in the region 1593-1617  $\text{cm}^{-1}$  in the IR spectra, and a sharp singlet at 8.29-8.68 ppm in proton NMR spectra of the compounds. The elemental analyses of the compounds are in agreement with the suggested composition of the compounds. The physical, spectroscopic and analytical data of the compounds are summarized in Tables 1 and 2.

**Table 1:** Physical and analytical data of the Schiff bases L1-L3

Compound	Formula	mp ( $^{\circ}\text{C}$ )	Yield (%)	Microanalysis % Calculated (Found)		
				C	H	N
L1	$\text{C}_{11}\text{H}_{10}\text{N}_4\text{O}$	234-236	87	61.67 (62.16)	4.71 (4.64)	26.15 (26.27)
L2	$\text{C}_{11}\text{H}_9\text{N}_3\text{O}_2$	223-225	40	61.39 (61.23)	4.22 (4.07)	19.53 (19.99)
L3	$\text{C}_{11}\text{H}_9\text{N}_3\text{OS}$	241-242	81	57.13 (57.64)	3.92 (3.85)	18.17 (18.93)

**Table 2:** Characteristic IR and NMR spectra data of L1-L3

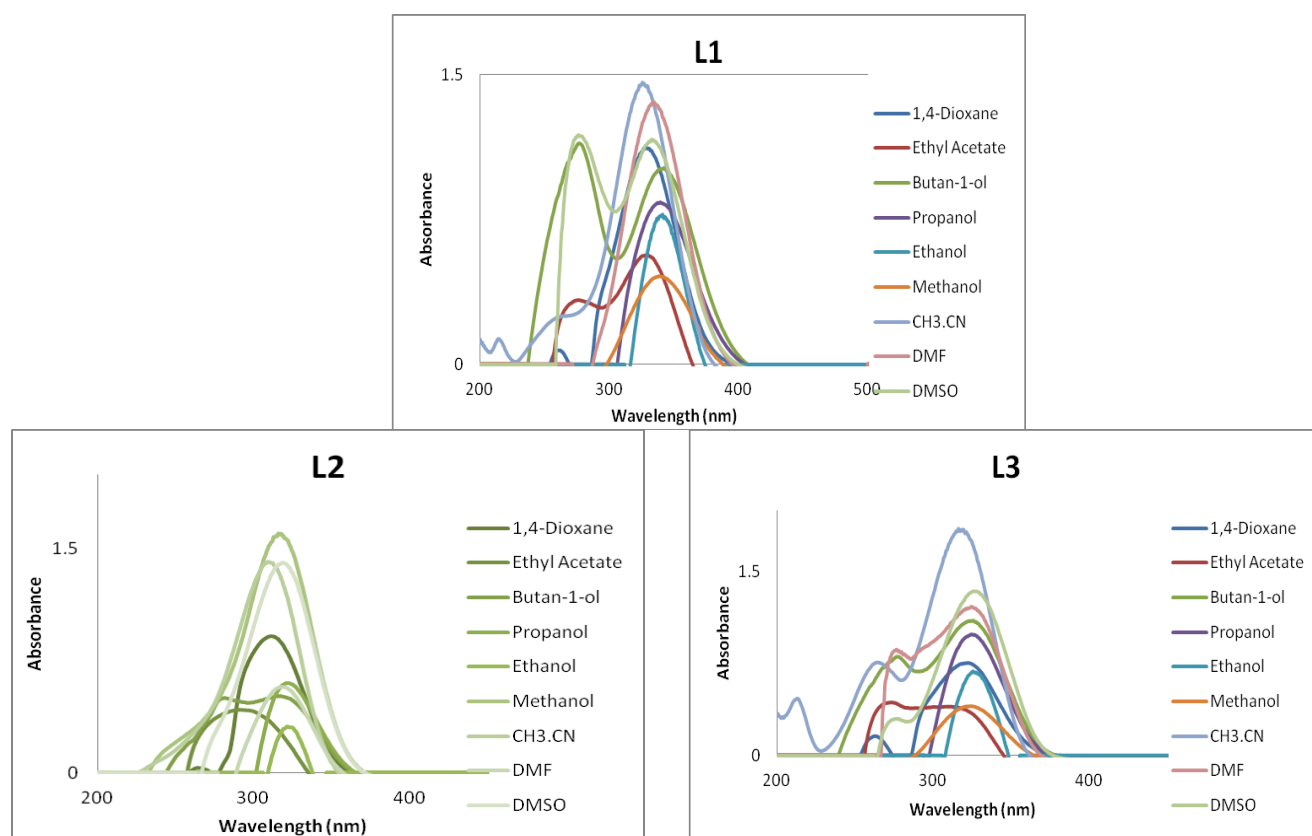
Compound	IR bands ( $\text{cm}^{-1}$ )			Chemical shift $\delta$ (ppm)	
	$\nu_{\text{NH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=N}}$	HC=N $\delta_{\text{H}}$	$\delta_{\text{C}}$
	L1	3056	1645	1594	8.29
L2	-	1644	1617	8.35	140.89
L3	3028	1661	1593	8.68	140.94

### Electronic Absorption Spectra

The absorption spectra of the Schiff bases were investigated in the wavelength range 200-500 nm using nine solvents of different polarities comprising of non-polar, polar protic and polar aprotic solvents. The wavelengths of maximum absorption and molar extinction coefficients of the investigated Schiff bases are summarized in Table 3. The absorption spectra of the compounds (Figure 1) consist of two main absorption bands. The band in the wavelength range 265-280 nm assigned to the  $\pi$ - $\pi^*$  electronic transition involving the imine functional group and aromatic ring. This band is insensitive to solvent polarity but can be affected by substitution at the aromatic rings [10]. The second band found in the wavelength range of 300 – 345 nm occurs in all solvents studied and is proposed to arise from the  $\pi$ - $\pi^*$  transition involving conjugation within the Schiff base system. The band is sensitive to solvent polarity and shifts to longer wavelength with increase in solvent polarity.

**Table 3:** Electronic absorption data for Schiff bases **L1-L3** in different solvents

	Dioxane	Ethyl Acetate	1-Butanol	1-Propanol	Ethanol	Methanol	Acetonitrile	DMF	DMSO
<b>L1</b>	261 (3.85) 329 (5.05)	276 (4.52) 328 (4.75)	277 (5.06) 343 (5.01)	340 (4.92)	341 (4.89)	340 (4.92)	214(4.11) 265 (4.98) 326 (5.16)	334 (5.13)	277 (5.08) 333 (5.07)
<b>L2</b>	269 (3.52) 312 (4.96)	300(4.62)	282 (4.69) 318 (4.71)	322 (4.78)	323 (4.49)	317 (5.20)	309 (5.15)	317 (4.76)	320 (5.15)
<b>L3</b>	263 (4.20) 322 (4.88)	273 (4.64) 307 (4.60)	278 (4.91) 326 (5.04)	323 (4.99)	326 (4.84)	324 (4.60)	213 (4.66) 265 (4.88) 318 (5.27)	277 (4.93) 325 (5.08)	277 (4.48) 328 (5.13)

**Fig 1:** The UV -vis absorption spectra of Schiff bases (**L1-L3**) in nine solvents

This bathochromic shift observed for the lower energy band is attributed to a greater stability of the excited state  $\pi^*$  orbital compared to the ground state  $\pi$  orbital in the compounds [11]. The shift in absorption maxima observed is in the order butanol > propanol > ethanol > methanol > DMSO > DMF > dioxane > ethyl acetate > acetonitrile.

The absorption maxima of the compounds in each solvent decrease in the order L1>L3>L2. This trend reflects the electron donating ability of the heteroatom present in the aldehydic ring. The nitrogen atom in pyrrole is a good electron donor, although sulphur and oxygen atoms are both group 16 elements, the higher electronegativity of oxygen makes it a poorer electron donor compared to sulphur. Thus, in each solvent **L2** containing the furan ring has the lowest absorption maxima.

The absorption spectra of molecules are influenced by physical properties of the solvent, change in polarity and dipole moment of the solute and solvation energy of the solute in the solvent. Hence, the spectral data reflects the solute-solvent interactions occurring with each solute-solvent pair.

In order to quantitatively assess the solvatochromic behaviour of the Schiff bases, linear solvation energy relationship (LSER) concepts developed by Kamlet-Taft [12] equation (1) and Catalan [13] equation (2) were utilized.

$$\lambda_{\max} = C_0 + C_1 f(n) + C_2 f(\epsilon) + C_3 \pi + C_4 \sigma$$

$$\lambda_{\max} = C'_0 + C'_1 \text{SPP} + C'_2 \text{SA} + C'_3 \text{SB} \quad (2)$$

The correlation of the spectroscopic data was carried out by multiple linear regression analysis using SPSS 15.0 statistical package. The Kamlet-Taft parameters for the solvents used and the experimental and calculated absorption frequencies for the lowest energy transition band are listed in Table 4, while the corresponding data using the Catalan parameters are listed in Table 5. Based on the statistical parameters, the LSER models obtained using both the Kamlet-Taft and Catalan parameters (Tables 6 and 7) are satisfactory with  $R^2$  values in the range 0.916-0.998. The coefficients  $C_0$  and  $C'_0$  in tables 6 and 7 indicate the wavenumbers for the absorption bands in the gaseous phase.  $C_1$  values represent the refractive index function and it is proportional to the induction dispersive interactions while  $C_2$  is the dielectric function which is proportional to the orientation interactions [14-15].

In **L1**, both  $C_1$  and  $C_2$  have positive values with  $C_1 > C_2$ , indicating negative solvatochromism that is, the ground state is more stable compared to the excited state with the transition controlled by solute values related to the inductive dispersive interactions. **L2** and **L3** both have negative values of all coefficients, this means the excited state of the compound is more stabilized than the ground state and the absorption band undergoes a bathochromic shift with increase in solvent polarity. The orientation interactions dominate the transition in L2 containing the highly electronegative oxygen atom.

The absolute value of  $C_4$  is the least in all compounds showing that the hydrogen bond donor ability of the solvent is least important in the correlation. All compounds possess electron donating N, O and S atoms which can give rise to stronger interaction between the solute and acidic solvent.

**Table 4:** LSER coefficients for Kamlet-Taft parameters and statistical parameters for **L1-L3**

Compound	$C_0$	$C_1$	$C_2$	$C_3$	$C_4$	$R^2$	R	P	No. of solvents
L1	30916.36	254.750	241.201	-1627.414	-653.225	0.977	0.954	0.006	9
L2	39781.91	-2149.450	-6723.014	-2167.226	-491.632	0.988	0.975	0.010	8
L3	37484.39	-7675.123	-4344.717	-1024.781	-493.373	0.998	0.990	0.06	7

**Table 5:** LSER coefficients for Catalan Parameters and Statistical Parameters for **L1-L3**

Compounds	$C'_0$	$C'_1$	$C'_2$	$C'_3$	$R^2$	R	P	No. of solvents
L1	31417.940	-145.214	-1518.933	-1874.313	0.975	0.951	0.011	9
L2	43565.183	-11060.100	-3201.143	-2114.941	0.916	0.840	0.046	8
L3	39857.524	-9087.000	-3190.627	-287.120	0.975	0.951	0.018	7

The LSER based on the Catalan model have negative values for all three correlation coefficients, thus indicating positive solvatochromism for the compounds. The low absolute value of  $C'_3$  obtained for the compounds reveal that factors controlling solvent basicity are not important in the absorption spectra and the absorption band would shift to lower energy with increasing basicity of solvent.

**Table 6** Kamlet-Taft parameters for solvents and the experimental and calculated wavenumbers for the selected  $\pi\pi^*$  transition

Solvents	Kamlet Taft parameters				$n_{\text{experimental}}$			$n_{\text{calculated}}$		
	$f(n)$	$f(\pi)$	$f(\sigma)$	$\rho$	L1	L2	L3	L1	L2	L3
1,4-Dioxane	0.254	0.287	0.37	0	30395.14	32051.28	31055.90	30448.14	36504.57	33908.81
Ethyl Acetate	0.227	0.625	0.45	0	30487.80	34129.69	32573.29	30392.60	34116.85	32565.54
1-Butanol	0.242	0.846	0.84	0.84	29154.52	31446.54	30674.85	29266.32	31340.63	30676.13
1-Propanol	0.235	0.866	0.9	0.84	29411.76	31055.90	30959.75	29171.72	31091.19	30581.47
Ethanol	0.221	0.887	0.75	0.86	29325.51	30959.75	30674.85	29404.27	31295.35	30741.54
Methanol	0.203	0.913	0.66	0.98	29411.76	31545.74	30864.20	29474.03	31295.29	30799.75
Acetonitrile	0.211	0.924	0.19	0.4	30674.85	32467.53	31446.54	30622.48	32507.89	31458.36
DMF	0.258	0.922	0.69	0	29940.12	31545.74	30769.23	30081.55	31533.35	30791.28
DMSO	0.283	0.938	0.76	0	30030.03	31250.00	30487.80	29977.86	31220.34	30458.15

**Table 7:** Catalan parameters for solvents and the experimental and calculated wavenumbers for the selected  $\pi\pi^*$  transition

Solvents	Catalan parameters			$n_{\text{experimental}}$			$n_{\text{calculated}}$		
	SPP	SA	SB	L1	L2	L3	L1	L2	L3
1,4-Dioxane	0.701	0	0.443	30395.14	32051.28	31055.90	30485.82	34875.13	30485.82
Ethyl Acetate	0.795	0	0.542	30487.80	34129.69	32573.29	30286.62	33626.11	30286.62
1-Butanol	0.837	0.341	0.809	29154.52	31446.54	30674.85	29262.12	31505.30	29262.12
1-Propanol	0.847	0.367	0.782	29411.76	31055.90	30959.75	29271.78	31368.57	29271.78
Ethanol	0.853	0.4	0.658	29325.51	30959.75	30674.85	29453.20	31458.83	29453.20
Methanol	0.857	0.605	0.545	29411.76	31545.74	30864.20	29353.04	30997.34	29353.04
Acetonitrile	0.895	0.044	0.286	30674.85	32467.53	31446.54	30685.09	32920.67	30685.09
DMF	0.954	0.031	0.613	29940.12	31545.74	30769.23	30083.37	31618.15	30083.37
DMSO	1	0.072	0.647	30030.03	31250.00	30487.80	29950.68	30906.23	29950.68

## CONCLUSION

The solvatochromic behaviour of heterocyclic Schiff bases of INH have been studied in various organic solvents of different polarity. The nature of the heteroatom had significant effect on the lower energy electronic transition. The pyrrole Schiff base showed negative solvatochromism while the furan and thiophene compounds exhibited positive solvatochromism. The hydrogen bond acceptor capability was more effective in directing the solvatochromic behavior of the compounds, The Catalan model proposed positive solvatochromism for all the compounds with the acidity of solvents most effective in controlling solute-solvent interaction.

## REFERENCES

1. T. M. Fasina, R. O. Dada, *J. Chem. Pharm. Res.*, **5**, 177 (2013).
2. D. Sriram, P. Yogeewari, N. S. Myneedu, V. Saraswat, *Bioorg Med Chem Lett.*, **16**, 2127 (2006).

3. K. R. Surati, *Spectrochimica Acta Part A: Mol. and Biomol. Spectro.*, **79**(1), 272 (2011).
4. Z. Guo, R. Xing, S. Liu, Z. Zhong, X. Ji, L. Wang, *Carbohydrate Res.*, **342** (10), 1329 (2007).
5. M. C. Lourenço, M. L. Ferreira, M. V. De Souza, M. A. Peralta, T. R. Vasconcelos, M. D. Henriques, *Eur. J. Med. Chem.*, **43**(6), 1344 (2008).
6. Y. G. Sidir, I. Sidir, E. Tasal, E. Ermis, *J. Mol. Liq.*, **162**, 148- (2011).
7. A. Ohshima, A. Momotake, T. Arai, *J. Photochem. Photobiol. A. Chemistry*, **162**, 475 (2004).
8. V. Mkpene, E. Essien, *American Chem. Sci.*, **8**, 1 (2015).
9. Y. G. Sidir, I. Sidir, H. Berber, G. Turkoylu, *J. Mol. Liq.*, **204**, 33 (2015).
10. A. A. Soliman, *Spectrochim. Acta A.*, **53**, 509 (1997).
11. H. H. Hammud, A. Ghannoum, M. S. Masoud, *Spectrochim. Acta A.*, **63**, 255 (2006).
12. M. J. Kamlet, R. W. Taft, *J. Am. Chem. Soc.* **98**, 377 (1976).
13. J. Catalan, *J. Phys. Chem. B.* **113**, 5951 (2009).
14. A. Airinei, E. Rusu, D. Dorohoi, *Spectrosc. Lett.* **34**, 65-74 (2001).
15. D. O. Dorohoi, A. Airinei, M. Dimitri, *Spectrochim. Acta A.*, **73**, 257 (2009).