Effect of substituents on infrared, H1 and C_{13}NMR spectra of Schiff's bases derived from Furfuryl amine

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ABSTRACT

Several substituted Schiff,s bases have been derived from furfuryl amine and their IR, 1H and 13C NMR spectra are recorded. The IR νC=N(cm-1), NMR δ(ppm) of CH=N spectral data have been correlated with Hammett substituent constants and Swain-Lupton's parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the above spectral data has been studied.

INTRODUCTION

Schiff's bases have attracted considerable attention in organic chemistry due to their significant biological activities like anticancer [1], antitumor [2], anti-inflammatory [3], insecticidal [4], antituberculosis [5], antimicrobial [6], anticonvulsant [7] activity. In the present day the correlation analysis of Schiff's bases have become one of the important studies for researchers to study their substituent effect. They are also known as 'azomethines', 'anils' or 'imines'. Among the large number of synthetic and naturally occurring nitrogen donor molecules, schiff bases are of the greatest interest recently, the correlation analysis of Schiff bases [Anils] have been reported [8-9]. The proton and carbon-13 nuclear magnetic resonance spectral studies have been applied to numerous structural problems.[10-14] Their use in structure parameter correlations have now become very popular. A similar study involving Anils is utmost unknown. Hence, several *ortho-*,*meta-* and *para*-substituted Anils were prepared and their infrared, proton and carbon-13 NMR resonance spectra were recorded with a view to study the structure parameters correlations in these newly synthesized Anils .

MATERIALS AND METHODS

General method for the preparation of anils
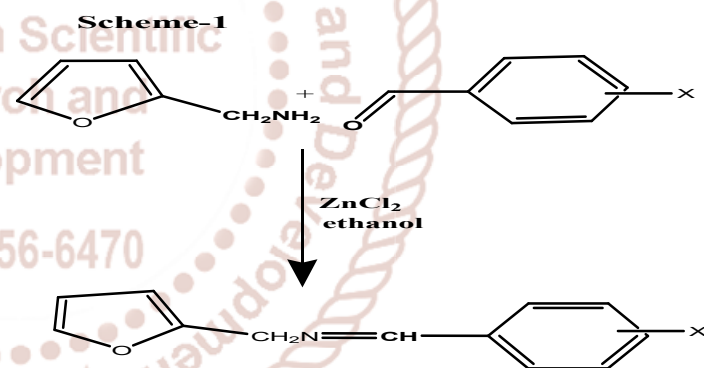
where X = H, *p*-OCH$_3$, *m*-OCH$_3$, *p*-NO$_2$, *m*-NO$_2$, *p*-CH$_3$, *m*-CH$_3$, *p*-Cl, *m*-Cl, *p*-Br.

The anils were prepared[15] by refluxing equimolar quantities of substituted benzaldehyde and Furfuryl amine in alcohol for about 2 to 3 hrs. The resulting solution was cooled and poured into the cold water. The precipitated anil was filtered, washed dried and recrystallized from alcohol. The purity of the anils were checked by determining their melting points

RESULTS AND DISCUSSION

IR SPECTRA

Normally Schiff's basesshow two C=N bands for syn and anti conformers in solution. Although an equilibrium mixture of different conformations of some of the Schiff's bases may exist in crystalline state. In addition to C=N the system under investigation also shows strong band due to the C-O-C group that is present in the furyl moiety of the system.

Effect of substituents on C=N stretching frequency

The C=N stretchitng frequencies of these newly synthesized Schiff's bases shows that when a powerful electron donating group is present the C=N stretchitng frequency shifted to lower wavelength region This may be due to the fact that electron donating group reduces the double bond character of the C=N band and thereby lower the frequency. Eventhough the effectiveness are similar in *meta* and *para* positions the increase in C=N absorption frequency is attributed to the loss of co-planarity of furyl system with the C=N group. The IR spectral values are given in Table(1) The data which are given in the Table-1 are sperately analysed through various correlation equations involving σ and σ +values .The results of statistical analysis are presented in Table -2

All the correlation data given in Table –2 are pertaining to single parameter equation which indicates clearly that poor correlation is obtained with Hammett σ and σ +constants..In view of the

inability of some sigma constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlation involving $\Box$I and $\Box$R constants. The correlation equations generated are shown in Table 3.

Table 1

C=N stretching frequencies of substituted Schiff's bases

S. No.	Substituents	$\Box_{C=N}$ (cm^{-1})
1.	*m*-OCH$_3$	1615.50
2.	*p*-CH$_3$	1613.47
3.	*p*-Cl	1628.64
4.	H	1629.81
5.	*m*- Cl	1628.26
6.	*p*-NO$_2$	1633.73
7.	*m*-CH$_3$	1615.06
8.	*p*-OCH$_3$	1613.57
9.	*m*-NO$_2$	1633.25
10	*p*-Br	1623.97

Table 2
Results of statistical analysis of C=N stretching frequencies of Schiff's bases

System	Constant for correlation	A	B	S.D	R	Substituent
$v_{C=N}$(nm)	σ	1625.5	4.107	2.8456	0.554	X = H, *m*-OCH$_3$, *p*-NO$_2$, *p*-OCH$_3$, *m*-Cl,*m*-CH$_3$ *p*-CH$_3$, *p*-Br, *m*-NO$_2$, *m*- CH$_3$
	σ^+	1626.6	2.245	3.0786	0.461	X = H, *m*-OCH$_3$, *p*-NO$_2$, *p*-OCH$_3$, *m*-Cl,, *m*-OCH$_3$,- *p*-CH$_3$, *p*-Br, *m*-NO$_2$

A = Intercept; B = Slope

Table 3
Correlation equation with σ_I and σ_R constants

System	Correlation equation in $\nu_{C=N}$ (cm^{-1})	Substituent
Schiff's bases	$\nu_{C=N}$ = 162.96 + 5.6906 σ_I + 6.5964 σ_R (R = 0.743, S.D = 2.255, n = 10	X = H, m-OCH$_3$, p-NO$_2$, p-OCH$_3$, m-Cl,m- CH$_3$ p-CH$_3$, p-Br, m-NO$_2$,p-Cl

^{1}H NMR spectra

There has been considerable interest in the literature in recent days to correlate chemical shifts of proton with substituent constants in various systems. In general, the signals for aromatic protons present in a molecule appear in the downfield region of around 7 ppm due to magnetic anisotropic effect. In most of the cases, since the absorption of the azomethine proton in the schiff's bases are also in the aromatic region, it is quite difficult to differentiate the olefinic protons signal from that of the aryl protons. In such cases it is essential to go for some other techniques like INDOR double resonance. Table 4 shows the 1 H-NMR chemical shifts of the methine protons (joined to C-α), the 13C-NMR chemical shifts of all the substituted schiff's bases respectively. A plot of the 1 H-NMR chemical shifts of the methine protons does not give a reasonable Hammett correlation, whereas there is such a correlation with the methine carbon. The extension of the effect to the methine protons is essentially a second order effect and we suggest that this accounts for the inadequate correlation. From the table-5 it is inferred that even the correlation with σI and σR parameters also produce only a poor correlation. This can be due to the nature of the system in which the benzene ring orients itself with an angle of 180ºto the plane of the molecule and also due to large distance between the protons under investigation and the substituents

Table 4
^{1}H NMR&^{13}C NMR chemical shifts (δH, δC in ppm) in substituted Schiff's bases

S. No.	Substituent	δH (ppm)	δ (ppm) C-α
1.	m-OCH$_3$	7.901	157.82
2.	p-CH$_3$	7.989	157.23
3.	m-Cl	7.849	159.25
4.	H	7.947	160.02
5.	m-CH$_3$	7.888	158.03
6.	p-OCH$_3$	8.225	158.41
7.	m-NO$_2$	8.788	167.80
8.	p-Br	8.128	159.94
9.	p-NO$_2$	8.360	169.75
10.	p-Cl	7.956	160.01

Table 5

Correlation equation with σ_I and σ_R

System	Correlation equation		Substituent
Schiff's base	δ_H (ppm) = 7.908 + 0.428119 σ_I H_β + 0.3986 σ_R 0.0855; SD = 0.7418; n = 10	R =	m-OCH₃, p-CH₃, m-Cl, H, m- CH₃, , p-OCH₃, p-Br, m-NO₂, , p-NO₂, , p-Cl

C13 NMR SPECTRA

There is an acceptable correlation with the 13C-NMR chemical shifts of C-α. The plot of 13C-NMR chemical shifts of C-α versus the Hammett constants gives an equation:
δC-α = (159.43 ± 0.58) + (11.57 ± 1.82)σp, where the value of the Hammett reaction constant ρ = +10.57 with a correlation coefficient of 0.9047 and standard deviation of 1.84 for n = 10. We suggest that the *p'*-substituents perturb the aldimine π-bond. This is corroborated by the multiple linear regression which considers the inductive (σI) and resonance (σR) dual parameters, and the chemical shifts for 13C-α, where a major contribution of the σR parameter is demonstrated. δC-α = (9.56 ± 2.73) σI + (10.36 ± 2.48) σR + (159.28 ± 0.95) n = 10 correlation coefficient (r) = 0.904 standard deviation (s) =1.953 The comparison of the relationships concerning δC-α with other results in the literature indicated similar chemical shifts considering the electronic effects. The substituted Schiff's bases showed an acceptable Hammett correlation with ρ = 4.06 (correlation coeficient = 0.922) and the 13C-NMR shifts of C-α were more largely affected in the Schiff base series (ρ = 10.57), Chemical shifts a (δH, δC in ppm), The results of statistical analysis of substituent effect of C α carbon is shown in Table 6 Since the correlations with Hammett substituent constants are very poor it was thought worthwhile to seek multiple correlations involving σ I and σ R constants.

δC-α = (9.56 ± 2.73) σI + (10.36 ± 2.48) σR + (159.28 ± 0.95) n = 10
correlation coefficient (r) = 0.904 standard deviation (s) =1.953

The derived Hammett substituent constants i) (σp) and dual parameters ii) (σI and σR) for substituted Schiff bases shows that normal substituent effect is operative in all systems.

Table 6
Results of statistical analysis of chemical shift C_α carbon of substituted Schiff's base

Systems	Types of carbon	Constants for correlation	R	I	ρ	S	N	Substitutent
	C_α	σ	0.1627	121.21	0.872	1.9018	10	m-OCH₃, p-CH₃, m-Cl, H, m- CH₃, , p-OCH₃, p-Br, m-NO₂, , p-NO₂, , p-Cl
		σ⁺	0.0577	121.42	0.219	2.2645	9	m-OCH₃, p-CH₃, m-Cl, H, p-OCH₃, p-Br, m-NO₂, , p-NO₂, , p-Cl

CONCLUSION

When correlations were made for C=N stretching frequencies with σ and $\sigma+$ constants only a fair correlation was obtained. The proton NMR correlated shifts (ppm) of the azomethine proton of the Schiff's basess investigated are assigned. Their correlations involving various substituent parameters give positive ρ values. The correlation of C13 NMR chemical shifts (ppm) of Cα with Hammett substiituents constants. σI and σR parameters collectively explain substituents effect in some cases.

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