

Effect of substituents on phenazine derivatives by spectral studies

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ABSTRACT

A series of eleven substituted dipyrido[3,2-a; 2',3'-c]phenazine derivatives have been synthesized and examined their purities by literature method. The infrared and ¹³C NMR spectral data of prepared phenazines were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis. From the results of statistical analysis, the effect of substituents on the infrared frequencies (ν , cm⁻¹) and ¹³C nmr chemical shifts(δ , ppm) has been studied.

Keywords: Phenazines; IR spectra; ¹³C NMR spectra; Spectral correlation; Hammett substituent constants; Swain-Lupton's parameter

1. INTRODUCTION

Phenazine and its derivatives are an important ligand for metal complex formation in inorganic chemistry[1]. Inorganic chemists paid much more attention for studying the complex formation[1], physico-chemical properties[2] and biological activities[3,4] of phenazine-metal complexes. Phenazine molecules possess part of quinoxaline moiety. Spectral studies of phenazine and its derivatives were made by Lue et al.[5]. Phenazine ligands were employed for the study of synthesis, enantiomeric resolution and binding interactions with calf thymus DNA of Cr(III) complex by Vasudevan et al.[6]. Interaction of Ru(II)-phenazine complex with CT-DNA study was made by Santos et al.[7]. The crystal structure, DNA cleavage activity of phenazine-Cu(II) complex was studied by Begum et al.[8]. The structure activity relationship of phototoxic Fe(III)-phenazine complex was reported by Saha et al.[9]. This phenazine ligand was applied for synthesizing Ru(II) Light Switch complexes[3], and its DNA-Binding[3], photo cleavage[4], spectral properties[1], DNA-Non covalent cross linking with nano particles[10], excited state behaviours in presence of nucleic acids[2], electronic properties[11], DNA mediated energy transfer[12], electrochemical characterization[13], metal based inhibitor of NEDD8-activating enzyme[14], tuned cell membrane affinity[15], synthesis of poly ketones[16], and photo oxidations[1]. Nair et al., have studied the optical properties of phenazine-Ru complexes [17]. Qsar and qspr study was established with various compounds such as chalcones [18], pyrazolines[19], imines[20], flavones[21], pyrimidines[22], carboxamides[23], oxazines[24], epoxides[25], sulfonamides[26], acyl bromides[27], Tröger's bases[28], di-imines[29] and thiadiazoles[30].

Thirunarayanan and Sekar was studied the spectral qsar correlations in the pyrazoline derivatives [31]. The correlation study of infrared and ^{13}C -NMR chemical shifts of aryl hydrazides with Hammett substituent constants and F and R parameters were established by Thirunarayanan et al.,[32] Mayavel et al., have investigated the spectral correlations-linearity of infrared and NMR spectral frequencies of carbazole imines with Hammett substituent constants, F and R parameters[33]. Sathiyendiran et al.[34] have prepared some 2-oxopropyl diazenyl benzoic acids and studied the spectral correlation. Recently Thirunarayanan et al have studied the spectral qsar study of phenazine derivatives[35]. There was no spectral correlation study was reported with phenazine molecules in the past. Therefore the author have taken efforts to prepare some substituted phenazines, recorded their infrared and ^{13}C NMR spectra for the spectral correlations study.

2. EXPERIMENTAL

2.1. General

Merck and Sigma-Aldrich branded chemicals were used in this present study. The infrared spectra of all phenazines were recorded in SHIMADUZ Fourier Transform IR spectrophotometer using KBr discs. The ^{13}C NMR spectra of all compounds have been recorded in BRUKER AV 400 type spectrometer, using CDCl_3 as a solvent, 100 MHz for ^{13}C NMR spectra, taking TMS as standard.

2.2. Synthesis of substituted phenazine derivatives

The substituted phenazines were synthesized and the purities of the compounds were examined by literature method [1, 29-31]. The general structure of the substituted phenazine is shown in Fig.1.

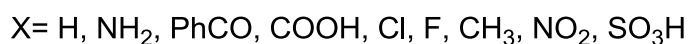
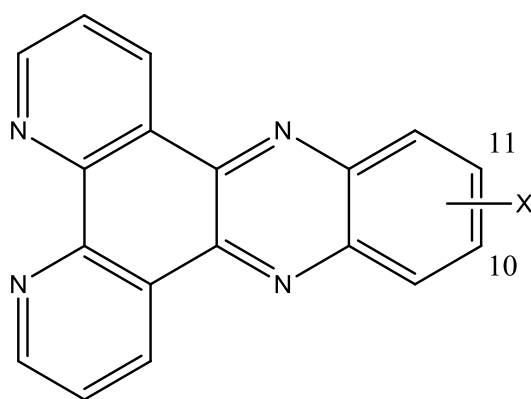


Fig. 1. General structure of substituted phenazines.

3. RESULTS AND DISCUSSION

In the present study, the authors have investigated the correlation of infrared and ^{13}C -NMR spectral data of 10- and 11-substituted phenazines with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. Present investigation compound structure was shown is Fig. 1. This phenazines are symmetric molecule without substituents. When introducing the substituents at 10 and 11th position, the symmetry will be disturbed. With respect to $\text{C}_{15}=\text{N}_{14}$ and $\text{C}_6=\text{N}_7$, the substituents attached in 11th position were considered as *meta*- and *para*- positions. Within the considerations, the authors have performed the assigned spectral frequencies were correlated separately with respect to $\text{C}_6=\text{N}_7$ and correlations performed with respect to $\text{C}_{15}=\text{N}_{14}$ systems in the phenazines.

3.1. Infrared spectral correlation

The assigned the C=N stretches (cm^{-1}) of the present investigation substituted phenazines were tabulated in Table 1. These data were correlated with Hammett substituent constants, F and R parameters [18-35]. In this correlation, the Hammett equation was employed as,

Table 1. The infrared C=N stretches (cm^{-1}) and ^{13}C chemical shifts(ppm) of substituted phenazines.

Sl. No.	X	$\nu\text{C}=\text{N}$	$\delta\text{CN}_{\text{Pyr}}$	$\delta\text{CN}_{\text{Phena}}$	$\delta\text{C}_{\text{ipso}}$
1	H	1577	149.54	153.85	130.87
2	NH_2	1574	149.38	153.74	146.33
3	PhCO	1548	149.41	153.82	138.14
4	COOH	1569	149.45	153.88	132.46
5	Cl	1578	149.62	153.89	143.75
6	F	1574	149.61	153.81	145.66
7	CH_3	1569	149.31	153.71	138.04
8	NO_2	1579	150.19	153.98	149.56
9	SO_3H	1566	149.63	153.76	146.36

$$\nu = \rho\sigma + \nu_0 \quad (1)$$

where ν_0 is the frequency for the parent member of the series.

The results of statistical analysis are tabulated in Table 2. From Table 2, the single parameter correlation of $\nu\text{C}=\text{N}$ *m*-substituted pattern phenazines gave satisfactory correlation coefficients with σ , σ^+ , σ_1 constants and F parameters. Hammett substituent constants, F and R parameters except fluoro-substituent for σ_1 and R parameter excluding PhCO substituent. The Hammett σ_R constants and R parameter were failing in correlations. Similarly the single parameter correlation of these stretches of *p*-substituted pattern phenazines gave satisfactory correlation with Hammett σ_R constants and F parameters. The Hammett σ , σ^+ , σ_1 constants and R parameters were failing in correlations. All correlations gave positive ρ values. This meant that the normal substituent effect operates in all systems. The failure in correlation was due to the inability of predicting the substituent effects on the frequencies along with the resonance conjugative structure as shown in Fig. 2.

Table 2. Results of statistical analysis of IR and ^{13}C NMR spectral values of substituted phenazines with Hammett σ , σ^+ , σ_I , σ_R constants, F and R parameters.

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
Correlations performed with <i>p</i> -substitution pattern							
$\nu\text{C}=\text{N}(\text{cm}^{-1})$	σ	0.818	1570.36	2.499	9.73	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.823	1570.36	3.624	9.67		
	σ_I	0.815	1568.13	5.603	9.64		
	σ_R	0.913	1569.43	12.336	9.01		
	F	0.923	1567.77	8.203	9.45		
	R	0.801	1569.71	0.415	9.76		
$\delta\text{CN}_{\text{pyre}}$ (ppm)	σ	0.971	149.42	0.623	0.19	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.960	149.49	0.467	0.21		
	σ_I	0.974	149.37	0.764	0.18		
	σ_R	0.907	149.57	0.252	0.26		
	F	0.964	149.38	0.603	0.21		
	R	0.914	149.58	0.143	0.27		
$\delta\text{CN}_{\text{phena}}$ (ppm)	σ	0.969	153.78	0.198	0.06	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.973	153.80	0.183	0.06		
	σ_I	0.972	153.76	0.245	0.06		
	σ_R	0.814	153.83	0.053	0.09		
	F	0.974	153.76	0.229	0.06		
	R	0.812	153.83	0.039	0.09		
$\delta\text{C}_{\text{ipso}}$ (ppm)	σ	0.905	144.87	1.723	10.19	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.913	145.11	4.052	10.09		
	σ_I	0.905	138.88	19.168	8.78		
	σ_R	0.942	143.97	17.66	9.21		
	F	0.957	138.23	19.945	8.32		
	R	0.969	142.84	25.202	7.31		
Correlations performed with <i>m</i> -substitution pattern							
$\nu\text{C}=\text{N}(\text{cm}^{-1})$	σ	0.901	1568.69	4.109	9.70	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.900	1569.77	0.132	9.76		
	σ_I	0.908	1567.88	6.992	9.58		
	σ_R	0.881	1568.95	14.939	9.21		
	F	0.928	1567.79	8.869	9.37		
	R	0.871	1519.75	0.415	9.72		
$\delta\text{CN}_{\text{pyre}}$ (ppm)	σ	0.992	149.35	0.833	0.16	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.961	149.49	0.389	0.21		
	σ_I	0.917	149.38	0.763	0.18		
	σ_R	0.827	149.58	0.293	0.27		
	F	0.905	149.25	0.501	0.22		
	R	0.804	149.58	0.143	0.27		
$\delta\text{CN}_{\text{phena}}$ (ppm)	σ	0.981	153.75	0.277	0.05	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.984	153.79	0.175	0.04		
	σ_I	0.981	153.78	0.274	0.05		
	σ_R	0.805	153.82	0.027	0.09		
	F	0.907	153.76	0.228	0.05		
	R	0.813	153.83	0.039	0.09		
$\delta\text{C}_{\text{ipso}}$ (ppm)	σ	0.911	142.87	6.734	9.23	9	H, -NH ₂ , -COPh, -COOH, -Cl, -F, CH ₃ , -NO ₂ , -SO ₃ H
	σ^+	0.901	143.47	5.067	9.96		
	σ_I	0.905	139.25	11.268	8.83		
	σ_R	0.915	142.25	28.791	8.31		
	F	0.950	139.32	17.711	8.49		
	R	0.969	142.84	25.531	7.31		

r=correlation coefficient; I= intercept; ρ =slope; s=standard deviation; n=number of correlated derivatives

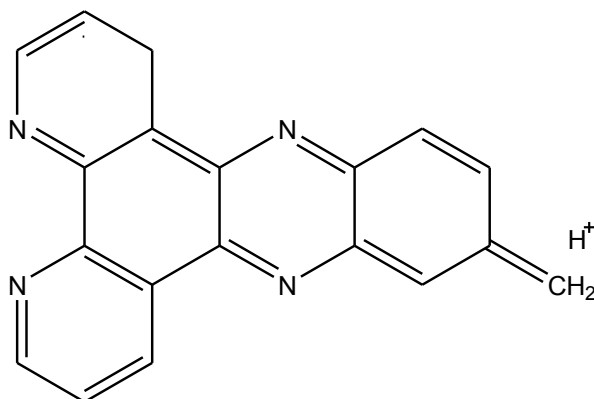


Fig. 2. The resonance-conjugative structure.

3.2. ^{13}C NMR spectral correlation

The ^{13}C NMR chemical shifts of CN pyridine and phenazines moieties were assigned and are presented in Table 1. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-regression analysis [18-35]. In these correlations, the Hammett equation was taken in the form as,

$$\delta = \delta_0 + \rho\sigma \quad (2)$$

Where δ_0 is the chemical shift of the corresponding parent compound.

The results of statistical analyses are shown in Table 2. The correlations performed with respect to CN (*m*-substitution pattern), chemical shifts of $\delta\text{C}=\text{N}_{\text{pyri}}$ and phena (ppm) gave satisfactory correlation with σ and σ^+ and σ_I constants F parameters gave satisfactory correlations except PHCO substituent. The Ipso carbon chemical shifts gave satisfactory correlation with Hammett substituent constants, F and R parameters. All correlations gave positive ρ values. These mean that the normal substituent effect operates in all systems. The reason for the failure in the correlation was already stated and along with the resonance conjugative structure as shown in Fig. 2.

The ipso carbon chemical shifts of the phenazines with Hammett σ_R constant and R parameters gave satisfactory correlations. The Hammett σ , σ^+ , σ_I constants and F parameter were fail in correlations. This is due to the inability of substituents along with conjugative structure as shown in Fig. 2.

The correlations performed with respect to CN (*p*-substitution pattern), chemical shifts of $\delta\text{C}=\text{N}_{\text{pyri}}$ (ppm) gave satisfactory correlation Hammett substituent constants, F and R parameters excluding PhCO substituent. The correlation of $\delta\text{C}=\text{N}_{\text{phena}}$ (ppm) with Hammett σ and σ^+ and σ_I constants F parameters. The σ_R and R parameters gave poor correlations for this chemical shifts. All correlations gave positive ρ values. These mean that the normal substituent effect operates in all systems. The reason for failure in correlation was already stated and it is associated with resonance conjugated structure as shown in Fig. 2. The Hammett gave satisfactory correlations except PHCO substituent. The Ipso carbon chemical shifts gave satisfactory correlation with Hammett substituent constants, F and R parameters.

In single parameter correlations, some of the sigma constants gave poor correlations with were failed in correlations with Hammett substituent constants, F and R parameters. They are worthwhile when seeking multi-linear correlations with σ_I and σ_R constants or Swain Lupton's[36] F and R parameters gave satisfactory correlations for infrared and ^{13}C NMR spectral data of phenazines. The generated multi-regression analysis equations are shown in (3-26)

Correlations performed with *m*-substitution pattern

$$\nu\text{C=N}(\text{cm}^{-1}) = 1567.71(\pm 5.071) + 4.800(\pm 1.401)\sigma_I + 13.634(\pm 1.875)\sigma_R \quad (3)$$

$$(R = 0.933, n = 9, P > 90\%)$$

$$\nu\text{C=N}(\text{cm}^{-1}) = 1567.76(\pm 4.832) + 9240(\pm 1.248)F + 2.651(\pm 1.428)R \quad (4)$$

$$(R = 0.928, n = 9, P > 90\%)$$

$$\delta\text{CN}_{\text{Pyri}}(\text{ppm}) = 149.36(\pm 0.085) + 0.844(\pm 0.023)\sigma_I + 0.522(\pm 0.038)\sigma_R \quad (5)$$

$$(R = 0.982, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Pyri}}(\text{ppm}) = 19.42(\pm 0.106) + 0.587(\pm 0.276)F + 0.338(\pm 0.016)R \quad (6)$$

$$(R = 0.966, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Phena}}(\text{ppm}) = 153.75(\pm 0.028) + 0.282(\pm 0.081)\sigma_I + 0.052(\pm 0.011)\sigma_R \quad (7)$$

$$(R = 0.981, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Phena}}(\text{ppm}) = 153.76(\pm 0.023) + 0.258(\pm 0.061)F + 0.124(\pm 0.069)R \quad (8)$$

$$(R = 0.986, n = 9, P > 95\%)$$

$$\delta\text{C}_{\text{ipso}}(\text{ppm}) = 134.19(\pm 6.400) + 8.501(\pm 1.621)\sigma_I - 42.971(\pm 20.204)\sigma_R \quad (9)$$

$$(R = 0.964, n = 10, P > 95\%)$$

$$\delta\text{C}_{\text{ipso}}(\text{ppm}) = 133.42(\pm 6.258) + 15.023(\pm 1.472)F - 29.343(\pm 13.708)R \quad (10)$$

$$(R = 0.968, n = 10, P > 95\%)$$

Correlations performed with *p*-substitution pattern

$$\nu\text{C=N}(\text{cm}^{-1}) = 1567.90(\pm 5.234) + 5.234(\pm 1.382)\sigma_I + 12.147(\pm 1.154)\sigma_R \quad (11)$$

$$(R = 0.934, n = 9, P > 90\%)$$

$$\nu\text{C=N}(\text{cm}^{-1}) = 1567.71(\pm 5.299) + 8.551(\pm 1.337)F + 1.621(\pm 0.143)R \quad (12)$$

$$(R = 0.968, n = 10, P > 95\%)$$

$$\delta\text{CN}_{\text{Pyra}}(\text{ppm}) = 149.35(\pm 0.097) + 0.772(\pm 0.253)\sigma_I + 0.279(\pm 0.028)\sigma_R \quad (13)$$

$$(R = 0.978, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Pyra}}(\text{ppm}) = 149.38(\pm 0.909) + 0.667(\pm 0.271)F + 0.302(\pm 0.029)R \quad (14)$$

$$(R = 0.971, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Phena}}(\text{ppm}) = 153.76(\pm 0.035) + 0.243(\pm 0.092)\sigma_I + 0.044(\pm 0.001)\sigma_R \quad (15)$$

$$(R = 0.973, n = 9, P > 95\%)$$

$$\delta\text{CN}_{\text{Phena}}(\text{ppm}) = 153.76(\pm 0.054) + 0.250(\pm 0.076)F + 0.099(\pm 0.008)R \quad (16)$$

$$(R = 0.980, n = 9, P > 95\%)$$

$$\delta\text{C}_{\text{ipso}}(\text{ppm}) = 138.51(\pm 4.406) + 18.662(\pm 1.637)\sigma_I + 16.998(\pm 1.272)\sigma_R \quad (17)$$

$$(R = 0.965, n = 9, P > 95\%)$$

$$\delta\text{C}_{\text{ipso}}(\text{ppm}) = 138.29(\pm 3.267) + 15.327(\pm 8.234)F + 21.850(\pm 8.741)R \quad (18)$$

$$(R = 0.982, n = 10, P > 92\%)$$

4. CONCLUSIONS

Totally nine substituted phenazines derivatives have been synthesized and their purities were examined by literature method. The infrared and ^{13}C NMR spectral frequencies of C=N, C-N and ipso carbons of the phenazines were assigned and correlated based on *m*- and *p*- substituted system with Hammett substituent constants, F and R parameters using single and multi-regression analysis. Most of the correlations gave satisfactory correlation coefficients.

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