Spectral LFER studies in some
N-(substituted phenyl) formamides

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A series of N-(substituted phenyl) formamides were synthesised by sulphated titania (TiO_2-SO_4^{2-}) catalyzed formylation of substituted anilines and formic acid in acetonitrile medium at room temperature. The synthesised formamide derivatives are characterized by their spectral data. The infrared νNH, CO (cm^{-1}) stretches, chemical shifts(δ, ppm) of NH, COH and ipso carbons(Ar-C-NH) were assigned and correlated with Hammett substituent constants using single and multi-regression analysis. From the results of statistical analyses, the effect of substituents on the spectral data have been studied.

Keywords: N-(Substituted phenyl)formamides; Sulphated titania(TiO_2-SO_4^{--}); IR and NMR spectra; Anilines; Hammett correlations.

1. INTRODUCTION

Formylation reactions are important and useful for the bond formation of C-N-C class and synthesis of various formamide derivatives. These valuable formamide intermediates are utilized for building of

medicinally important compounds such as purines [1, 2]. The formyl skeleton moiety was an important amino protecting group in peptide synthetic methodologies [3, 4]. Formamide derivatives possess important biological activities such as fungicides [5], daptomycin antibiotics [6] and antioxidant [7]. Numerous solvent assisted, neat and solvent free formylation methods including microwave and ultrasonics have been reported [5–21] for synthesis of formamide derivatives. These synthetic formylation methods proceeds with or without catalysts such as Lewis acids[6], $ZnCl_2$[6], $SnCl_2$ [6], $LaCl_2$ [6], $La(OTf)_3$ [6], $FeCl_3$ [6], $AlCl_3$ [6], $NiCl_2$ [6], hydroxylamine hydrochlorie [7], neutral 1-butyl-3-methylimida-zolium tetrafluoroborate(Bmim)BF_4 [11], guanidine derived ionic liquids [12], ZnO [15], silica supported perchloric acid [16], silica-sulphuric acid [18], nano cerium oxide [19], natural HEU zeolite [20], I_2 [21], polyethylene glycol-400(PEG-400) [22], acetic formic anhydride[23], chloral [24], DCC [25], EDCl [26], activated formic esters[27], KF-Al_2O_3 [28], ammonium formate [29], CMDT [30], iridum [31], thiamine hydrochloride [32], sulphated titania (TiO_2-SO_4^{2-}) [33], sodium formate [22], sulphated tungstae [34], amberlite IR-120 [35] and melamine trisulfonic acid [36]. Spectroscopic data were useful for prediction of geometric and stereo isomeric structure of organic compounds [37, 38]. Infrared spectroscopic data was applied for prediction of ground state equilibrium of carbonyl compounds, acyl halides and ω-substituted esters [39-41]. Proton NMR chemical shifts (δ, ppm) are used for prediction of E or Z configuration of unsaturated systems and spatial arrangement of protons in alicyclic and heterocyclic system [42, 43]. The effect of substituents on some (E)-[4-(substituted benzylidene amino) phenyl] (phenyl) methanones were studied through spectral data with Hammett substituent constants by Mayavel et al., [44]. Thirunarayanan et al., have studied the effect of substituents on phenazine and quinoxaline derivatives using spectral data [45, 46]. The effect of substituents on triazole system was investigated through spectral data by Senbagam et al., [47]. Recently, Kable et al reported the geometrical and spatial arrangement of protons of some N-substituted phenyl formamides [11]. Within the above view, there is no report available for the study of spectral LFER on N-substituted phenyl formamides. Hence, the authors have taken efforts for study the spectral LFER on N-substituted phenyl formamides using their infrared and NMR spectroscopic data.

2. MATERIALS AND METHODS

2.1. General

Chemicals used in this work were procured from Sigma-Aldrich and E-Merck companies. Infrared spectra of all formamides were recorded in AVATAR-300 Fourier transform spectrophotometer. Bruker AV400 NMR spectrometer operating at 400 MHz has been utilized for recording ^{1}H NMR spectra and 100 MHz for ^{13}C NMR spectra in DMSO solvent using TMS as internal standard.

2.1.1. Preparation of N-(substituted phenyl) formamides

The N-(substituted phenyl) formamides were prepared by literature procedure [33, 39]. Mixture of substituted anilines (1 mmol) and formic acid (3 mmol) were stirred with 0.1g of TiO_2-SO_4^{2-} catalyst in acetonitrile at room temperature for 30 m. The completion of reaction was monitored by TLC. After completion of the reaction the product was separated by extraction method with 10mL of DCM.   The general structure of the N-(substituted phenyl) formamides are shown in Fig. 1.
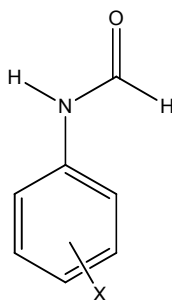
X= H, 4-COOH, 3-CN, 4-Br, 2-Cl, 3-Cl, 4-Cl, 4-F, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$

Fig. 1. General structure of N-(substituted phenyl) formamides

The purities of all formamides were checked with their physical constants and spectroscopic data as early reported [8,33, 39]. The infrared and NMR spectroscopic data of all prepared N-(substituted phenyl) formamides are presented in Table 1.

Table 1. Infrared (ν, cm⁻¹), NMR (δ, ppm) and mass spectral data of N-(substituted phenyl) formamides.

Sl. No.	X	IR [ν, cm⁻¹]		¹H NMR [δ, ppm]			¹³C NMR [δ, ppm]			Mass [m/z]
		NH	CO	NH	COH		COH	Ar-C-N [ipso]		
1	H	3261	1700	9.177	8.330		163.24	159.94		120.90
2	4-Br	3268	1695	9.168	8.364		163.58	159.85		197.89
3	4-COOH	3276	1685	9.065	8.269		163.29	159.53		164.09
4	2-Cl	3309	1664	9.012	8.312		163.22	159.65		154.06
5	3-Cl	3312	1671	9.122	8.325		163.56	159.84		154.05
6	4-Cl	3266	1662	9.325	8.302		163.32	159.88		154.08
7	3-CN	3305	1665	9.205	8.420		163.36	159.26		145.09
8	4-F	3288	1676	9.210	8.324		163.31	159.36		138.06
9	2-OH	3346	1662	9.221	8.325		163.25	159.21		136.07
10	4-OH	3256	1658	9.215	8.213		163.33	159.25		136.08
11	4-OCH₃	3258	1644	9.101	8.195		163.15	159.18		150.08
12	4-CH₃	3259	1648	9.115	8.134		163.23	159.23		134.10
13	3-NO₂	3292	1706	9.362	8.431		163.62	159.93		165.04
14	4-NO₂	3294	1699	9.358	8.434		163.63	159.96		165.12

3. RESULTS AND DISCUSSION

3.1. Infrared spectral correlation

The assigned infrared νNH and CO(cm^{-1}) stretches of N-(substituted phenyl) formamides were correlated with Hammett σ, σ$^+$, σ$_I$, σ$_R$ constants, F and R parameters using single and multi-regression analysis [37, 38, 40–50]. In this infrared stretches correlation, the Hammett equation was employed as,

$$\lambda = \rho\sigma + \lambda_0 \qquad\qquad (1)$$

where λ$_0$ is the frequency for the parent member of the series.

The results of statistical analysis are presented in Table 2. From the Table 2, νNH (cm^{-1}) stretches of N-(substituted phenyl) formamides correlated satisfactorily with Hammett σ, σ$^+$ and σ$_I$ constants. The field and resonance factors of the substituents were fail in correlations. All correlations gave positive ρ values. This implies that there is normal substituent effects operates in all systems. The failure in correlation was due to the inability of prediction of substituent effect on the NH stretches of formamides and associated with resonance-conjugative structure as illustrated in Fig. 2.
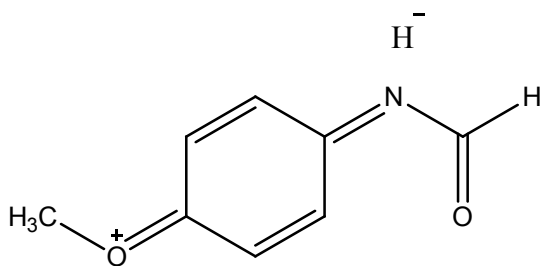

Fig. 2. The resonance-conjugative structure

The correlation of νCO (cm^{-1}) stretches of N-(substituted phenyl) formamides gave satisfactorily correlation with Hammett σ, σ$^+$, σ$_I$, σ$_R$ constants, F and R parameters.

Table 2. Results of statistical analysis of IR and NMR spectral data of N-(substituted phenyl) formamides with Hammett σ, σ^+, σ_I, σ_R constants, F and R parameters.

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
νC=N [cm^{-1}]	σ	0.902	3281.44	20.144	26.40		
	σ^+	0.903	3283.17	17.133	25.76		H, 4-Br, 4-COOH, 2-Cl, 3-Cl,
	σ_I	0.903	3267.77	46.548	25.46	14	4-Cl, 3-CN, 4-F, 2-OH, 4-OH,
	σ_R	0.811	3282.75	12.946	27.35		4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	F	0.836	3266.47	45.830	25.61		
	R	0.804	3284.21	3.881	27.53		
νC=O [cm^{-1}]	σ	0.906	1669.43	33.924	16.00		
	σ^+	0.906	1671.32	24.404	15.55		H, 4-Br, 4-COOH, 2-Cl, 3-Cl,
	σ_I	0.906	1661.24	33.324	19.40	14	4-Cl, 3-CN, 4-F, 2-OH, 4-OH,
	σ_R	0.905	1681.85	45.635	17.11		4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	F	0.903	1660.30	33.987	19.42		
	R	0.905	1680.81	34.173	17.02		
δNH [ppm]	σ	0.838	9.196	0.107	0.10		
	σ^+	0.822	9.184	0.044	0.10		H, 4-Br, 4-COOH, 2-Cl, 3-Cl,
	σ_I	0.904	9.106	0.129	0.09	14	4-Cl, 3-CN, 4-F, 2-OH, 4-OH,
	σ_R	0.830	9.212	0.212	0.10		4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	F	0.842	9.103	0.218	0.09		
	R	0.810	9.910	0.332	0.10		

cont. Table 2.

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
δCH [ppm]	σ	0.907	8.279	0.186	0.05	14	H, 4-Br, 4-COOH, 2-Cl, 3-Cl, 4-Cl, 3-CN, 4-F, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ^+	0.907	8.299	0.127	0.05		
	σ_I	0.907	8.129	0.305	0.06		
	σ_R	0.905	8.345	0.186	0.07		
	F	0.906	8.204	0.217	0.07		
	R	0.845	8.336	0.118	0.08		
δCO [ppm]	σ	0.907	163.30	0.308	0.12	14	H, 4-Br, 4-COOH, 2-Cl, 3-Cl, 4-Cl, 3-CN, 4-F, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ^+	0.906	163.34	0.194	0.12		
	σ_I	0.906	163.17	0.491	0.12		
	σ_R	0.905	163.42	0.339	0.14		
	F	0.905	163.18	0.431	0.11		
	R	0.839	163.40	0.189	0.15		
δCN$_{ipso}$ [ppm]	σ	0.905	159.48	0.502	0.26	14	H, 4-Br, 4-COOH, 2-Cl, 3-Cl, 4-Cl, 3-CN, 4-F, 2-OH, 4-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ^+	0.906	159.38	0.386	0.24		
	σ_I	0.835	159.38	0.154	0.30		
	σ_R	0.905	159.69	0.714	0.27		
	F	0.820	159.45	0.308	0.32		
	R	0.905	159.67	0.510	0.27		

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

In single parameter correlations, some of the νNH (cm^{-1}) stretches of N-(substituted phenyl) formamides gave poor correlations with Hammett σ_R constant F and R parameters. While seeking in multi-parameter correlations of νNH and CO (cm^{-1}) stretches of N-(substituted phenyl) formamides with σ_I, σ_R constants or F and R Swain-Lupton's [50] parameters, they gave satisfactory correlation coefficients. The generated multi-linear regression analysis equations are given in (2–5):

$$\nu NH[cm^{-1}] = 3258.81\ (\pm 16.871) + 56.140(\pm 3.441)\sigma_I +$$
$$+ 29.721(\pm 2.980)\ \sigma_R \qquad (2)$$
$$(R = 0.945,\ n = 14,\ P > 90\%)$$

$$\nu NH[cm^{-1}] = 3264.41(\pm 16.849) + 47.201(\pm 34.85)F +$$
$$+ 7.423(\pm 2.216)R \qquad (3)$$
$$(R = 0.938,\ n = 14,\ P > 90\%)$$

$$\nu CO[cm^{-1}] = 1673.62(\pm 11.421) + 19.293(\pm 2.316)\sigma_I +$$
$$+ 40.555(\pm 2.225)\ \sigma_R \qquad (4)$$
$$(R = 0.960,\ n = 14,\ P > 95\%)$$

$$\nu CO[cm^{-1}] = 1669.18(\pm 10.527) + 27.733(\pm 2.177)F +$$
$$+ 32.092(\pm 1.308)R \qquad (5)$$
$$(R = 0.964,\ n = 14,\ P > 95\%)$$

3.2. NMR spectral correlation

The NMR chemical shifts of NH, CH, CO and ArC-N$_{ipso}$ (δ, ppm) of all the synthesized N-(substituted phenyl) formamides have been assigned and are presented in Table 1. Attempts have been made to correlate these chemical shifts (ppm) with Hammett σ, σ^+, σ_I, σ_R constants, F and R parameters using single and multi-regression analyses[37, 38, 40-50] for studying the reactivity through substituent effects. In this NMR chemical shifts (δ, ppm) correlations, the Hammett equation was applied in the form of (6):

$$\delta = \delta_0 + \rho\sigma \qquad (6)$$

where δ_0 is the chemical shift of unsubstituted system.

3.3. ^1H NMR spectral correlation

The ^{1}H NMR chemical shifts of NH and CH (δ, ppm) of all the synthesized N-(substituted phenyl) formamides have been made to

correlate with Hammett σ, σ$^+$, σ$_I$, σ$_R$ constants, F and R parameters using single and multi-regression analyses [28-32] and are presented in Table 2. From the Table 2, the correlation of NH chemical shifts (δ, ppm) gave satisfactory correlation with Hammett σ$_I$ constant only. The remaining Hammett σ, σ$^+$, σ$_R$ constants, F and R parameters were fail in correlations. The positive ρ values were obtained in all correlations. This means that there is normal substituent an effect operates in all systems. The reason for failure in correlation was already stated and associated with the resonance-conjugative structure as illustrated in Fig. 2.

The correlation of CH chemical shifts (δ, ppm) of substituted formamides gave satisfactory correlation with Hammett σ, σ$^+$, σ$_I$, σ$_R$ constants and F parameters. The R parameter was fail in correlation. In all correlations, there is a ρ values were observed and it indicates that the normal substituent effect operates in all systems. The reason for failure in correlation was already stated and associated with the resonance-conjugative structure as illustrated in Fig. 2.

In single parameter correlations, some of the ^{1}H NMR chemical shifts of NH and CH (δ, ppm) of all the synthesized N-(substituted phenyl) formamides were failing for production of correlation coefficients. They are worthwhile when seeking in the multi-regression analysis. All multi-regression analysis gave satisfactory correlation co-efficients and the regression equations are given in (7-10):

$$\Delta nh[ppm] = 9.130 (\pm 0.065) + 0.191(\pm 0.133)\sigma_I +$$
$$+ 0.079(\pm 0.001) \sigma_R \qquad (7)$$
$$(R = 0.948, n = 14, P > 90\%)$$

$$\delta NH[ppm] = 9.108(\pm 0.065) + 0.208(\pm 0.016)F +$$
$$+ 0.017(\pm 0.008)R \qquad (8)$$
$$(R = 0.943, n = 14, P > 90\%)$$

$$\delta CH[ppm] = 8.232(\pm 0.036) + 0.264(\pm 0.074)\sigma_I +$$
$$+0.116(\pm 0.064) \sigma_R \qquad (9)$$
$$(R = 0.981, n = 14, P > 95\%)$$

$$\delta CH[ppm] = 8.232 (\pm 0.040) + 0.248(\pm 0.081)F +$$
$$+ 0.099(\pm 0.005)R \quad (10)$$
$$(R = 0.974, n = 14, P > 95\%)$$

3.4. 13C NMR spectral correlation

The ^{13}C NMR chemical shifts of Ar-CN$_{ipso}$ CO (δ, ppm) of all the synthesized N-(substituted phenyl) formamides have been made to correlate with Hammett σ, σ^+, σ_I, σ_R constants, F and R parameters using single and multi-regression analyses [37, 38, 40–50]. The results of statistical analyses are presented in Table 2. From the Table 2, the correlation of CO chemical shifts (δ, ppm) gave satisfactory correlation with Hammett σ, σ^+, σ_I, σ_R constants and F parameters. The R parameter was fail in correlations. A positive ρ values were obtained for all correlations. This means that there is normal substituent an effect operates in all systems. The reason for failure in correlation was already stated and associated with resonance-conjugative structure as illustrated in Fig. 2.

The correlation of CO chemical shifts (δ, ppm) of substituted formamides gave satisfactory correlation with Hammett σ, σ^+, σ_R constants and R parameters. The Hammett σ_I constant and F parameter gave poor correlation. The ρ values were observed in all correlations and it indicates that the normal substituent an effect operates in all systems. The reason for failure in correlation was already stated and associated with resonance-conjugative structure as illustrated in Fig. 2.

In single parameter correlations, some of the ^{13}C NMR chemical shifts of ArC-N$_{ipso}$ and CO (δ, ppm) of all the synthesized N-(substituted phenyl) formamides were failing for production of correlation coefficients. When seeking in multi-correlations, they are worthwhile and producing satisfactory correlation co-efficients. The generated multi-regression equations are given in (11-14):

$$\delta CO(ppm) = 163.27(\pm 0.078) + 0.411(\pm 0.155)\sigma_I +$$
$$+ 0.231(\pm 139)\,\sigma_R \qquad (11)$$
$$(R = 0.973,\ n = 14,\ P > 90\%)$$

$$\delta CO(ppm) = 163.23(\pm 0.085) + 0.402(\pm 0.175)F +$$
$$+ 0.159(\pm 0.111)R \qquad (12)$$
$$(R = 0.943,\ n = 14,\ P > 90\%)$$

$$\delta CN_{ipso}(ppm) = 159.57(\pm 0.188) + 0.294(\pm 0.037)\sigma_I +$$
$$+ 0.633(\pm 0.032)\,\sigma_R \qquad (13)$$
$$(R = 0.959,\ n = 14,\ P > 95\%)$$

$$\delta CN_{ipso}(ppm) = 159.58(\pm 0.181) + 0.261(\pm 0.037)F +$$
$$+ 0.494(\pm 0.023)R \qquad (14)$$
$$(R = 0.955, \text{ n} = 14, \text{ P} > 95\%)$$

4. CONCLUSIONS

Totally fourteen N-(substituted phenyl) formamides were synthesised by sulphated titania (TiO$_2$-SO$_4^{2-}$) catalyzed formylation of substituted anilines and formic acid in acetonitrile medium at room temperature. The synthesised formamide derivatives are characterized by their physical constants and spectral data reported in earlier. The infrared νNH, CO (cm^{-1}) stretches, chemical shifts(δ, ppm) of NH, COH and ipso carbons(Ar-C-NH) were assigned and correlated with Hammett substituent constants using single and multi-regression analysis. From the results of statistical analyses, many of the single regression analysis of the assigned spectral data gave satisfactory correlations. All correlations gave positive ρ values and are supported for the normal substituent effect operates in all systems. All multi-regression analysis gave satisfactory correlations with spectral data of formamides.

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