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Research Article

APPLICATION OF HAMMETT EQUATION ON SPECTROSCOPIC DATA OF SOME ARYL SULPHONAMIDES

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ABSTRACT

Some N-(4-Chloro-1-naphthyl) substituted benzene sulphonamides have been synthesized by Ultrasound assisted condensation of 4-chloro-1-naphthylamine with various benzene sulfonyl chlorides in ethanol medium in room temperature. Infrared and NMR spectra of these sulphonamides were recorded. From the infrared spectra the SO_2 and NH vibrations (ν, cm^{-1}) were assigned. From the NMR spectra, the chemical shifts (δ, ppm) of NH protons and C-N carbons were assigned. These data were correlated with Hammett equation and various electronic effect coefficients through regression analysis. From the statistical analysis findings, the prediction of influence of electronic effects on the above functionalities in the sulphonamides was discussed.

Keywords: N-(4-chloro-1-naphthyl) substituted benzene sulphonamides, Ultrasonication, Hammett equation.

1. INTRODUCTION

Sulphonamides are the organo nitrogen-sulphur compounds containing -SO_2-NH- moieties between alkyl-alkyl or alkyl-aryl or aryl-aryl groups. They possess numerous pharmaceutical and medicinal activities illustratively ideal sulpha drugs, antibacterial, antifungal, and antioxidants [1-3]. Hammett QSAR and QPR linear relationships are very useful for analyzing the influence of substituents on the functional groups of the compounds through statistical single and multi-regression analysis [4-6]. This analysis was studied from the spectral data or kinetic data or equilibrium constants or medicinal or pharmaceutical data with Hammett electronic coefficients through both single and multi-regression equations [7, 8]. Infrared functional vibrations such as NH, SO_2 and NMR chemical shifts were subjected to investigate this study. Thirunarayanan and his co-workers investigated the regression analysis of functional group vibrations and NMR chemical sifts of various organic substrates. Recently, Muthuvel et al., [9] have predicted the electronic effects on the spectral functionalities on 4-(substituted phenyl sulphonamide) benzoic acids and they observed satisfactory and poor correlation coefficients. Complete literature inspection reveals that there is a non-accountable report visible for this type of investigations with N-(4-chloro-1-naphthyl) substituted benzene sulphonamides. Hence, authors engaged and exerted for analyzing the electronic effects of substituents on the spectral functionalities of said compounds by preparing and recording IR and NMR spectras.

2. MATERIALS AND METHODS

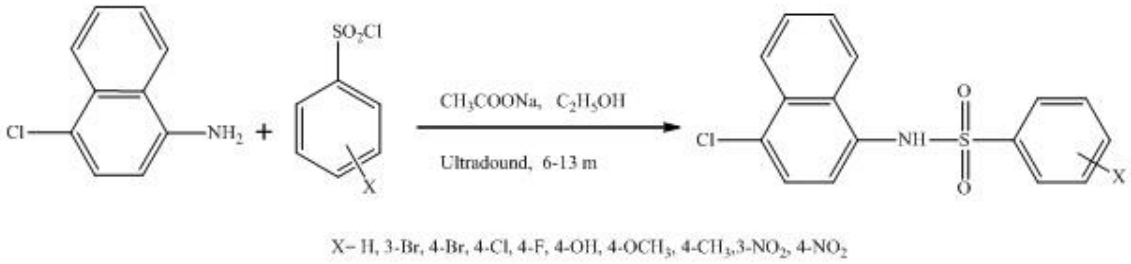
2.1. General

Chemicals employed in this investigation were procured from Sigma-Aldrich Chemical company. The melting points of the sulphonamides were determined in open capillaries method. The Shimadzu spectrophotometer in KBr disc was utilized for recording infrared spectra. The Bruker AV 400 and 500 spectrometers were employed for recording NMR spectra of all sulphonamides in DMSO solvent using TMS as standard. Thermo Finnigan CHN analyzer was used for finding the micro analysis of all sulphonamides.

2.2. Typical procedure for synthesis of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides

An equimolar quantity of 4-chloro-1-naphthylamine and various substituted benzene sulfonyl chlorides, 20 mL of ethanol and 0.5 mL of 1M sodium acetate were Ultrasonicated (CITIZEN Ultrasonicator, 120W, 40Hz, 240V, Ac) for 8-15 minutes at the room temperature (Scheme 1).

The solid mass was filtered and brine, distilled water and re-crystallized in ethanol. Characterization of synthesized products was done using melting points, molecular weights, yield, analytical as well as spectroscopic data. The analytical and physical coefficients of the sulphonamides were presented in Table 1.



X– H, 3-Br, 4-Br, 4-Cl, 4-F, 4-OH, 4-OCH_3, 4-CH_3,3-NO_2, 4-NO_2

Scheme 1: Synthesis of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides

3. RESULTS AND DISCUSSION

The NH and SO_2 vibrations (ν, cm^{-1}), NH and CN chemical shifts (δ, ppm) of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides were predicted from the spectra and tabulated in Table 2. The predicted frequencies are correlated by Hammett equation with electronic coefficients using statistical regression analysis [2-9].

Table 1.The analytical, physical coefficients and mass fragments (m/z) of the sulphonamides

Entry	X	M.F.	M.W.	Time (m)	Yield (%)	m.p. (˚C)	Mass(m/z)
1	H	$C_{16}H_{12}ClNO_2S$	318	8	93	113-114	318[M^+], 320[M^{2+}], 282, 240, 176, 161, 156, 126, 79, 77, 35, 15
2	3-Br	$C_{16}H_{11}BrClO_2S$	396	12	91	124-125	396[M^+], 398[M^{2+}], 400[M^{4+}], 360, 316, 240, 234, 218, 176, 161, 155, 126, 79, 77, 64, 35, 15
3	4-Br	$C_{16}H_{11}BrClO_2S$	396	10	92	124-125	396[M^+], 398[M^{2+}], 400[M^{4+}], 360, 316, 240, 234, 218, 176, 161, 155, 126, 79, 76, 77, 64, 35, 15
4	4-Cl	$C_{16}H_{11}Cl_2NO_2S$	352	9	90	118-119	352[M^+], 354[M^{2+}], 356[M^{4+}], 316, 240, 190, 176, 161, 126, 111, 77, 64, 35, 15
5	4-F	$C_{16}H_{11}ClFNO_2S$	336	13	90	131-132	336[M^+], 338[M^{2+}], 340[M^{4+}], 316, 240, 176, 174, 161, 159, 126, 95, 79, 64, 35,19, 15
6	4-OH	$C_{16}H_{12}ClNO_3S$	334	9	90	106-107	334[M^+], 336[M^{2+}], 316, 298, 281, 240, 176, 172, 161, 157, 155,140, 93, 76, 35, 17, 15
7	4-OCH_3	$C_{16}H_{14}ClNO_3S$	348	9	96	128-129	348[M^+], 350[M^{2+}], 332, 316, 312, 240, 186, 176, 171, 161, 107, 91,79, 77, 64, 35, 31, 15
8	4-CH_3	$C_{16}H_{14}ClNO_2S$	332	9	93	143-144	332[M^+], 334[M^{2+}], 316, 281, 240, 186, 176, 155, 140, 126, 107, 91,76, 64, 35, 15
9	3-NO_2	$C_{16}H_{11}ClN_2O_4S$	363	15	90	119-120	363[M^+], 365[M^{2+}], 316, 327, 240, 201, 186, 176, 161, 126, 122, 79, 76, 64, 46, 35, 15
10	4-NO_2	$C_{16}H_{11}ClN_2O_4S$	363	15	90	132-133	363[M^+], 365[M^{2+}], 316, 327, 240, 201, 186, 176, 161, 126, 122, 79, 76, 64, 46, 35, 15

Table 2: Vibrational and NMR spectroscopic data of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides

Entry	X	IR (ν, cm^{-1})		NMR (δ, ppm)	
		NH	SO_2	NH	CN
1	H	3322	1336	10.38	168.74
2	3-Br	3318	1330	10.34	168.68
3	4-Br	3334	1334	10.36	168.71
4	4-Cl	3329	1337	10.21	168.70
5	4-F	3341	1335	10.14	168.72
6	4-OH	3330	1331	10.11	168.73
7	4-OCH_3	3312	1328	9.87	168.55
8	4-CH_3	3318	1332	10.04	168.61
9	3-NO_2	3346	1346	10.83	168.94
10	4-NO_2	3348	1349	10.91	168.98

In vibrational spectral regression analysis, the Hammett equation was utilized as

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

Here ν is the infrared frequency of characteristic group frequencies of substituted system, ν_o is the infrared frequencies of characteristic group frequencies of unsubstituted system, ρ is the reaction coefficient which is dependent on the reaction conditions and σ substituent constants.

Single regression computations of NH and SO_2 (ν, cm^{-1}) vibrational frequencies with Hammett correlation was presented in Table 3.

The NH vibrations of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides gave satisfactory correlations with Hammett electronic substituent coefficients, F and R parameters.

Table 3: Single regression computations NH and SO_2 vibrations (ν, cm^{-1}), NH and CN chemical shifts (δ, ppm) of N-(4-chloro-1-naphthyl) substituted benzene sulphonamides Hammett substituted electronic coefficients.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
NH	σ	0.907	3325.41	22.346	9.26	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.906	3328.26	93.187	10.29		
	σ_I	0.907	3316.32	32547	9.18		
	σ_R	0.905	3334.11	36.426	10.69		
	F	0.907	3315.27	40.297	9.11		
	R	0.905	3334.85	25.341	11.10		
SO_2	σ	0.908	1333.08	14.137	4.01	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.907	1335.09	8.558	4.81		
	σ_I	0.905	1329.74	16.553	5.84		
	σ_R	0.908	1339.64	28.843	3.80		
	F	0.905	1329.20	17.981	5.81		
	R	0.908	1339.89	20.428	4.31		
NH	σ	0.908	10.17	0.724	0.17	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.908	10.28	0.455	0.20		
	σ_I	0.906	10.00	0.862	0.27		
	σ_R	0.908	10.51	1.441	0.17		
	F	0.906	9.65	0.985	0.27		
	R	0.907	19.51	0.989	0.21		
CN	σ	0.907	168.68	0.263	0.08	10	H, 3-Br, 4-Br, 4-Cl, 4-F, 4-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.906	168.72	0.153	0.10		
	σ_I	0.906	168.60	0.351	0.10		
	σ_R	0.907	168.04	0.509	0.08		
	F	0.906	168.59	0.390	0.10		
	R	0.906	168.80	0.390	0.10		

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

The positive ρ values were found to all regressions and it denotes that the normal electronic effects activate on the NH vibrations. Among the correlations, the sigma constants, inductive effect and filed components seems better than polar and resonance constants.

The SO_2 vibrations provided acceptable correlation coefficients in all single parameter regressions along with positive rho values. Here, the sigma and resonance electronic component seems better than other constants.

In magnetic resonance spectral data regressions, the utilized Hammett equation is shown in equation 2:

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

Here δ is the chemical shifts (δ, ppm) of characteristic group of substituted system, $\delta_o$is the chemical shifts (δ, ppm) of characteristic group of unsubstituted system, ρ is the reaction constant which is dependent on the reaction conditions and σ substituent constants.

The predicted ^1H and ^{13}C NMR chemical shifts (δ, ppm) of NH and CN data were presented in Table 2.

These chemical shifts (δ, ppm) are subjected to regression analysis using Hammett equation. The outcomes of the statistical regression analyses were as presented in Table 3. All sulfonamides gave satisfactory correlations for the predicted NH magnetic resonance data. Here the positive rho values were observed, and it denoted the normal electronic effects activates in NH functionality. The obtained regression coefficients were better for sigma, polar and resonance components.

The regressions of predicted CN chemical shifts (δ, ppm) of the sulfonamides gave acceptable correlations with positive rho values. In these correlations, the correlation coefficients were better for sigma and resonance components.

In multi-regression analysis [8, 9] both vibrational and NMR and infrared spectroscopic data of the sulfonamides gave acceptable regression coefficients and the corresponding computed equations are summarized in 3-10.

$$NH(\nu, cm^{-1}) = 3321.85(\pm 6.136) + 30.433(\pm 12.396)\sigma_I + 23.968(\pm 10.141)\sigma_R \quad (3)$$
(R=0.980; n=10; P>95%)

$$NH(\nu, cm^{-1}) = 3320.53(\pm 6.361) + 34.573(\pm 13.037)F + 17.105(\pm 10.935)R \quad (4)$$
(R=0.980; n=10; P>95%)

$$SO_2(\nu, cm^{-1}) = 1335.67(\pm 2.399) + 9.444(\pm 4.848)\sigma_I + 24.977(\pm 5.814)\sigma_R \quad (5)$$
(R=0.990; n=10; P>95%)

$$SO_2(\nu, cm^{-1}) = 1334.88(\pm 2.699) + 12.099(\pm 5.326)F + 17.583(\pm 4.633)R \quad (6)$$
(R=0.988; n=10; P>95%)

$$NH(\delta, ppm) = 10.295(\pm 0.093) + 0.511(\pm 0.189)\sigma_I + 1.232(\pm 0.227)\sigma_R \quad (7)$$
(R=0.993; n=10; P>95%)

$$NH(\delta, ppm) = 10.244(\pm 0.121) + 0.658(\pm 0.247)F + 0.834(\pm 0.207)R \quad (8)$$
(R=0.990; n=10; P>95%)

$$CN(\delta, ppm) = 168.706(\pm 0.054) + 0.233(\pm 0.109)\sigma_I + 0.414(\pm 0.131\sigma_R \quad (9)$$
(R=0.986; n=10; P>95%)

$$CN(\delta, ppm) = 168.68(\pm 0.061) + 0300(\pm 0.125)F + 0.269(\pm 0.105)R \quad (10)$$
(R=0.9894; n=10; P>95%)

4. CONCLUSION

Using ultrasonication method about ten N-(4-chloro-1-naphthyl) substituted benzene sulfonamides were prepared. These were analyzed by physical and spectral parameters. Predicted infrared NH and SO_2 (ν, cm^{-1}) vibrations, NH, and CN magnetic resonance parameters (δ, ppm) of the sulfonamides were subjected to regression computations with Hammett equation and analysis sigma, F and R values. All regressions gave acceptable regression coefficients with Hammett equation with Hammett electronic substituent constants, F and R parameters in all sulphonamides.

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