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IR and NMR spectral LFER study on 3-benzoicacid based sulfonamides

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ABSTRACT

A series containing nine 3-(substituted phenylsulfonamido)benzoicacids) have been synthesized and examined their purities by their data reported earlier. The characteristic infrared (ν_{NH}, $\nu_{SO(as)}$, $\nu_{SO(sym)}$ and $\nu_{CO(as)}$ cm^{-1}) stretches, NMR chemical shifts (δ, ppm) of NH protons, CO carbons were assigned and correlated with Hammett substituent constants and Swain-Lupton's parameters using single and multi-regression analysis. From the results of regression analysis the effect of substituents on the spectral data have been studied.

***Keywords*:** 3-(substituted phenylsulfonamido)benzoic acids; IR and NMR spectra; Correlation analysis

1. INTRODUCTION

Sulfonamides have been used as a protecting groups for amino groups [1], because the electron withdrawing effect, high stability, and ease of formation [2]. Sulfonamides are shown wide range of biological activities such as anti-viral, anti-inflammatory and anti-cancer activities [3]. A variety of methods for the construction of S–N bonds provide the available routes to obtain sulfonamides. Conventionally, sulfonamides can be synthesized by the nucleophilic substitution of primary or secondary amines to sulfonyl chlorides [4,5].

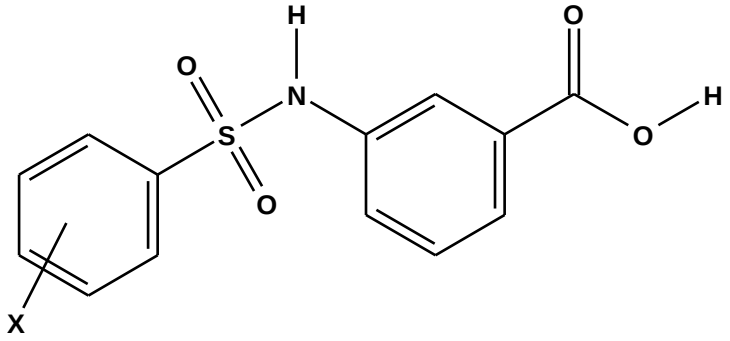
Researchers were synthesized sulfonamides using numerous catalysts such as K_2CO_3 [6], $NaHCO_3$ [7], DABCO [8], I_2/TBHP [9], β-Cyclodextrin [10], water [11], pyridine [12], PPh_3 [13], CsF-Celite [14], MgO [15], CuO [16], CdO [17], ZnO [18] and silica gel [19]. Similarly the effect of substituents were extensively studied compounds like 1-acetyl pyrazolines containing C=O [20], oxazine derivatives [21], sulfonamides [22] containing N–H were studied. That significant double-bond character exists in the S-N bond of sulfonamides. Furthermore, the necessity for rehybridization helps to explain the remarkably low basicity which the sulfonamide nitrogen displays. In effect, the basic electron pair is presumed to have significant π-bond character in addition to having been pulled strongly toward the sulfur by the latter's powerful inductive force. Protonation necessarily results in the complete destruction of the partial double bond and restores the electron pair to the nitrogen nucleus as a considerably more rigid and localized σ N–H bond [23]. Correlation study was useful for prediction of ground state configuration of organic substrates, mechanism of reaction intermediates, enone-enol tautomerism, structure-activity relationships of pharmaceutical compounds, effects of substituent of functional groups of organic substrates. G. Thirunarayanan and his co-workers have also studied through spectral data of many organic compounds and its effect of substituents on many heterocyclic compounds [24,25]. Recently, Senbagm et al., have studied the substituent effects on some triazole imines [26]. However no information has been found in the literature in the recent past, for the study of effect of substituents on sulfonamide group frequencies.

2. EXPERIMENTAL

2. 1. General

The chemicals used in this investigation were purchased from the Sigma-Aldrich, Alfa Aesar and E-Merck chemical companies. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on OMNIC Fourier-transform spectrophotometer. Bruker AV400 and 500 NMR spectrometer operating at 400 and 500 MHz was used to record ^1H and ^{13}C NMR spectra in DMSO solvent using TMS as internal standard.

2. 2. Synthesis of 3-(substituted phenylsulfonamido)benzoic acids



X = H, 4-Cl, 4-Br, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2

Figure 1. The general structure of 3-(substituted phenylsulfonamido)benzoicacid compounds

In the present investigation compounds 3-(substituted phenylsulfonamido)benzoic acids were prepared from literature method [27]. The purities of these sulfonamides were examined by data reported earlier in literature. The general structure of 3-(substituted phenylsulfonamido) benzoic acid was illustrated in Figure. 1. The analytical and physical constants of the sulfonamides are presented in Table 1.

3. RESULTS AND DISCUSSION

3. 1. Infrared spectral correlations

In the present study, the effect of substituents on the infrared stretching frequency values (ν_{NH}, $\nu_{SO(as)}$, $\nu_{SO(sym)}$ and $\nu_{CO(as)}$ cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acids were assigned and correlated with Hammett substituent constants and Swain-Lupton's [28] parameters using single and multi-regression analysis. In infrared spectral correlations, the Hammett equation was employed as

$$\nu = \rho\,\sigma + \nu_o \qquad \ldots (1)$$

where ν_o is the frequency of the parent compound.

The assigned ν_{NH}, ν_{CO}, $\nu_{SO(as)}$, $\nu_{SO(sym)}$ (cm^{-1}) stretches of 3-(substituted phenyl sulfonamido)benzoic acids are presented in Table 1. These frequencies were correlated with Hammett substituent constants and Swain-Lupton's [28] parameters using single and multi-regression analysis [29-32]. The results of statistical analyses are presented in Table 2.

Table 1. The infrared spectral NH, CO, $SO_{(sym)}$, $SO_{(asy)}$ (ν, cm^{-1}) stretches, NMR chemical shifts (δ, ppm) of NH protons, CO carbons of 3-(substituted phenylsulfonamido)benzoic acids.

S. No	X	IR (ν, cm^{-1})				^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)
		NH	CO	SO (sym)	SO (as)	NH	CO
1	H	3260.8	1339.0	1114.8	1683.9	10.547	167.21
2	4-Br	3254.5	1337.6	1159.3	1685.8	10.626	167.17
3	4-Cl	3259.8	1337.9	1160.2	1685.7	10.624	167.17
4	2-F	3250.3	1327.2	1164.0	1690.1	10.468	171.58
5	4-F	3359.7	1331.4	1161.0	1691.6	10.406	171.53
6	4-OCH_3	3256.9	1336.5	1157.4	1683.1	10.410	167.24
7	4-CH_3	3240.4	1346.2	1178.2	1693.5	10.880	171.50
8	2-NO_2	3300.3	1339.2	1175.0	1681.9	10.984	171.53
9	4-NO_2	3256.7	1338.5	1168.0	1680.1	10.936	170.26

Table 2. Results of statistical analysis of IR and NMR spectral data of of 3-(substitutedphenyl sulfonamido)benzoic acids with Hammett σ, σ^+, σ_I, σ_R constants, *F* and *R* parameters.

Frequency (cm^{-1})	Constants	r	I	ρ	s	n	Correlated derivatives
ν_{NH}	σ	0.713	3268.21	13.459	39.26	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ^+	0.803	3270.61	2.715	39.60	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_I	0.841	3247.92	59.442	36.08	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_R	0.822	3265.37	-33.591	38.61	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	F	0.848	3243.91	61.191	34.62	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	R	0.822	3264.53	-28.034	38.63	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
$\nu_{SO(as)}$	σ	0.905	1337.22	-0.823	5.65	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3
	σ^+	0.819	1337.37	-1.997	5.55	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3,4-CH_3, 2-NO_2, 4-NO_2
	σ_I	0.905	1341.08	-10.367	4.88	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3
	σ_R	0.906	1339.44	14.167	4.23	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3,4-CH_3
	F	0.907	1342.8	-12.959	3.92	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3
	R	0.906	1339.76	11.671	4.29	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3
$\nu_{SO(sym)}$	σ	0.831	1156.57	15.213	18.60	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ^+	0.821	1158.56	7.55	19.14	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_I	0.843	1147.61	31.248	17.59	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2

	σ_R	0.800	1159.71	-0.295	19.59	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	F	0.843	1147.68	27.241	17.61	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	R	0.805	1159.03	-3.149	19.57	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
$\nu_{(C=O)}$	σ	0.905	1687.58	-6.642	4.11	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ^+	0.903	1686.66	-2.979	4.62	8	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_I	0.835	1688.67	-6.389	4.58	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_R	0.905	1684.33	-10.948	3.96	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	F	0.808	1686.75	-1.285	4.89	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	R	0.905	1684.07	-9.085	3.981	7	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3,4-CH_3, 2-NO_2, 4-NO_2
δ_{NH}	σ	0.965	10.571	0.391	0.18	8	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 2-NO_2, 4-NO_2
	σ^+	0.905	10.616	0.231	0.20	7	H, 4-Br, 4-Cl, 4-F, 4-OCH_3, 2-NO_2, 4-NO_2
	σ_I	0.815	10.601	0.133	0.23	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_R	0.958	10.785	0.784	0.12	7	4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 2-NO_2, 4-NO_2
	F	0.804	10.667	-0.032	0.24	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	R	0.948	10.801	0.638	0.13	7	4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 2-NO_2, 4-NO_2
δ_{CO}	σ	0.832	169.06	1.895	2.21	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ^+	0.834	169.23	1.450	2.19	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2

	σ_I	0.826	168.57	2.278	2.25	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	σ_R	0.802	169.42	-0.22	2.33	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2
	F	0.904	167.92	3.47	2.06	7	H, 4-Br, 4-Cl, 4-F, 4-OCH_3, 2-NO_2, 4-NO_2
	R	0.806	169.36	-0.44	2.33	9	H, 4-Br, 4-Cl, 2-F, 4-F, 4-OCH_3, 4-CH_3, 2-NO_2, 4-NO_2

r – Correlation coefficient; I – intercept; ρ – slope; s – standard deviation; n – number of substituent.

The results of the statistical analysis [29-32] are presented in Table 2, it is evident that the infrared stretching frequency ν_{NH} (cm^{-1}) values of all the 3-(substituted phenylsulfonamido)benzoic acid compounds have shown poor correlations with the Hammett substituent constants σ, σ^+, σ_I, σ_R constants, *F* and *R* parameters. This is attributed to the weak inductive, field and resonance effects of the substituents for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Figure 2.

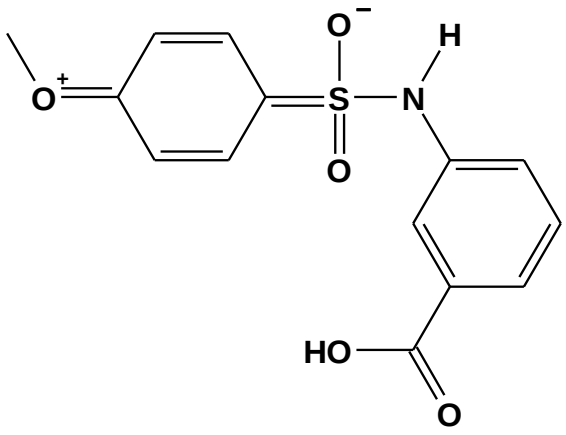


Figure 2. Resonance-conjugative structure

All the correlations with Hammett substituent constants viz., σ, σ^+, σ_I and F parameters have shown positive ρ values. This is indicates the operation of normal substituent effect with respect to infrared frequency (ν_{NH}, cm^{-1}) values of 3-(substituted phenylsulfonamido)benzoic acids compounds. The single linear plot of IR frequency ν_{NH} (cm^{-1}) values against Hammett constant σ , σ^+ is shown in the following Figure 3 and Figure 4.

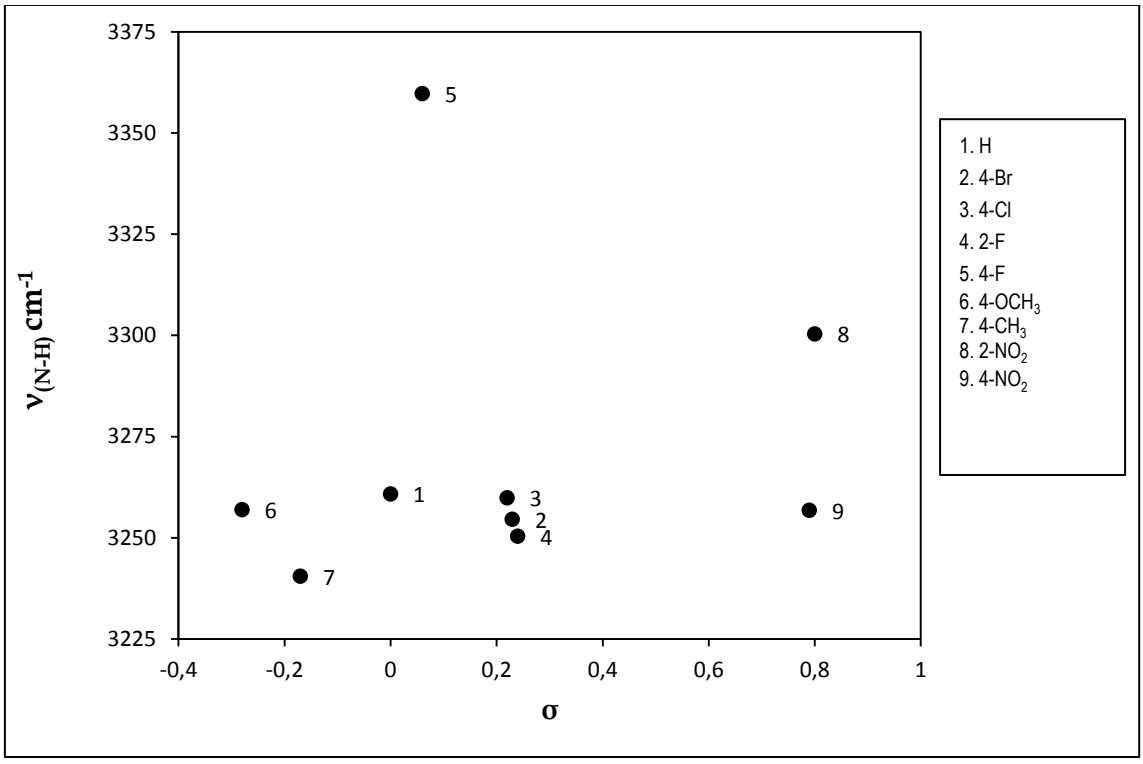


Figure 3. Single linear plot of ν_{N-H} (cm^{-1}) of substituted 3-(substituted phenylsulfonamido) benzoicacid compounds *versus* σ

Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (2) and (3).

$$\nu_{NH}\ (cm^{-1}) = 3241.08(\pm 25.630) + 61.136(\pm 5.501)\sigma_I - 36.646(\pm 3.552)\sigma_R \quad \ldots (2)$$
$$(R = 0.948,\ n = 9,\ P > 90\%)$$

$$\nu_{NH}\ (cm^{-1}) = 3241.97(\pm 24.013) + 57.785(\pm 5.674)F - 14.853(\pm 45.552)R \quad \ldots (3)$$
$$(R = 0.950,\ n = 9,\ P > 95\%)$$

The result of statistical analysis are presented in Table 2, it is evident that the infrared frequency ($\nu_{SO(as)}$, cm^{-1}) values of all the 3-(substituted phenylsulfonamido)benzoic acid compounds except those with 2-NO_2 and 4-NO_2 substituent, have shown satisfactory correlation with Hammett constants σ (r = 0.905), σ_I (r = 0.905) and σ_R (r = 0.906), parameters *F* (r = 0.907) and *R* (r = 0.906). When these substituents that have been given exception are included in regression they reduce the correlations considerably. The infrared frequency ($\nu_{SO(as)}$, cm^{-1}) values of 3-(substituted phenylsulfonamido)benzoic acid compounds have shown poor correlations (r < 0.900) with the Hammett substituent constant σ^+.

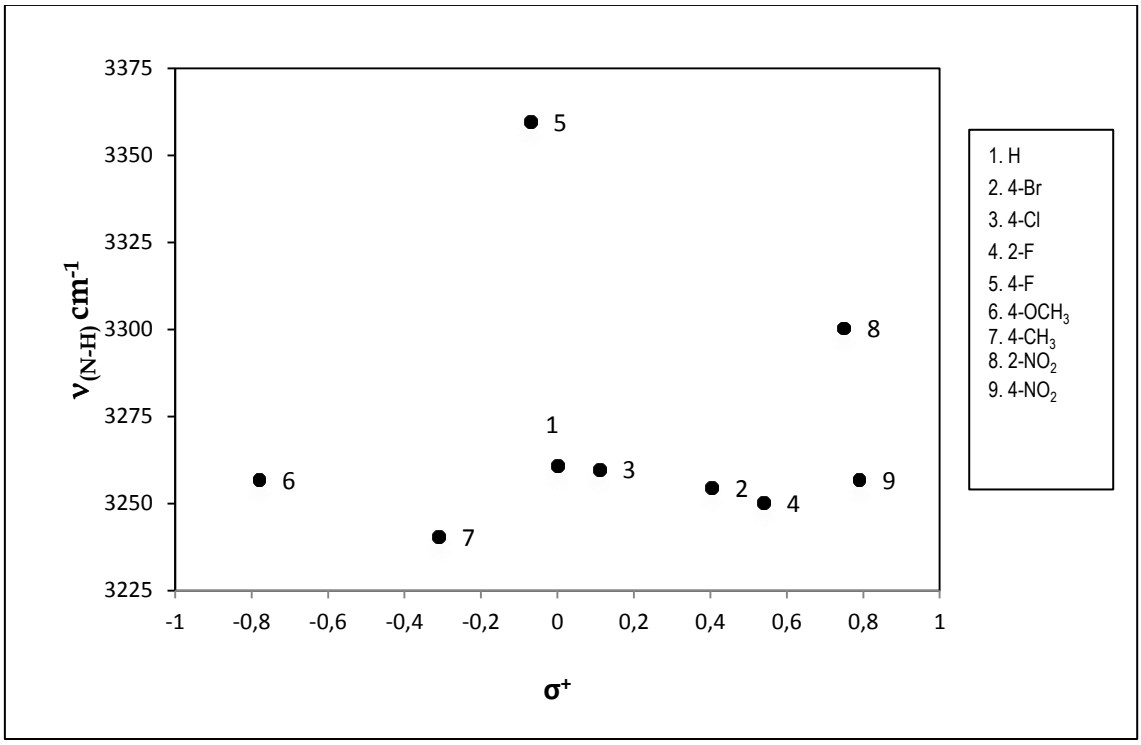


Figure 4. Single linear plot of ν_{N-H} (cm^{-1}) of substituted 3-(substituted phenylsulfonamido) benzoicacid compounds *versus* σ^+

All the correlations with Hammett substituent constant viz., σ, σ^+, σ_I and *F* parameters have shown negative ρ values. This is indicates the operation of reverse substituent effect with respect to infrared frequency ($\nu_{SO(as)}$, cm^{-1}) values of substituted 3-(phenylsulfonamido)benzoic acid compounds. The single linear plot of IR frequency ($\nu_{SO(as)}$, cm^{-1}) values against Hammett constant σ and σ^+ is shown in the following Figure 5 and Figure 6. Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (4) and (5).

$$\nu_{SO(as)}\ (cm^{-1}) = 1343.83(\pm 2.173) - 11.047(\pm 4.368)\sigma_I + 14.719(\pm 4.542)\sigma_R \quad \ldots (4)$$
$$(R = 0.985,\ n = 9,\ P > 95\%)$$

$$\nu_{SO(as)}\ (cm^{-1}) = 1344.00(\pm 1.901) - 10.850(\pm 3.617)F + 9.196(\pm 3.607)R \quad \ldots (5)$$
$$(R = 0.987,\ n = 9,\ P > 95\%)$$

The result of statistical analysis are presented in Table 2, it is evident that the infrared frequency ($\nu_{SO(sym)}$, cm^{-1}) values of all the 3-(substituted phenylsulfonamido)benzoic acid compounds have shown poor correlations with the Hammett substituent constants σ, σ^+, σ_I, σ_R constants, *F* and *R* parameters. This is attributed to the weak inductive, field and resonance effects of the substituents for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Figure 2.

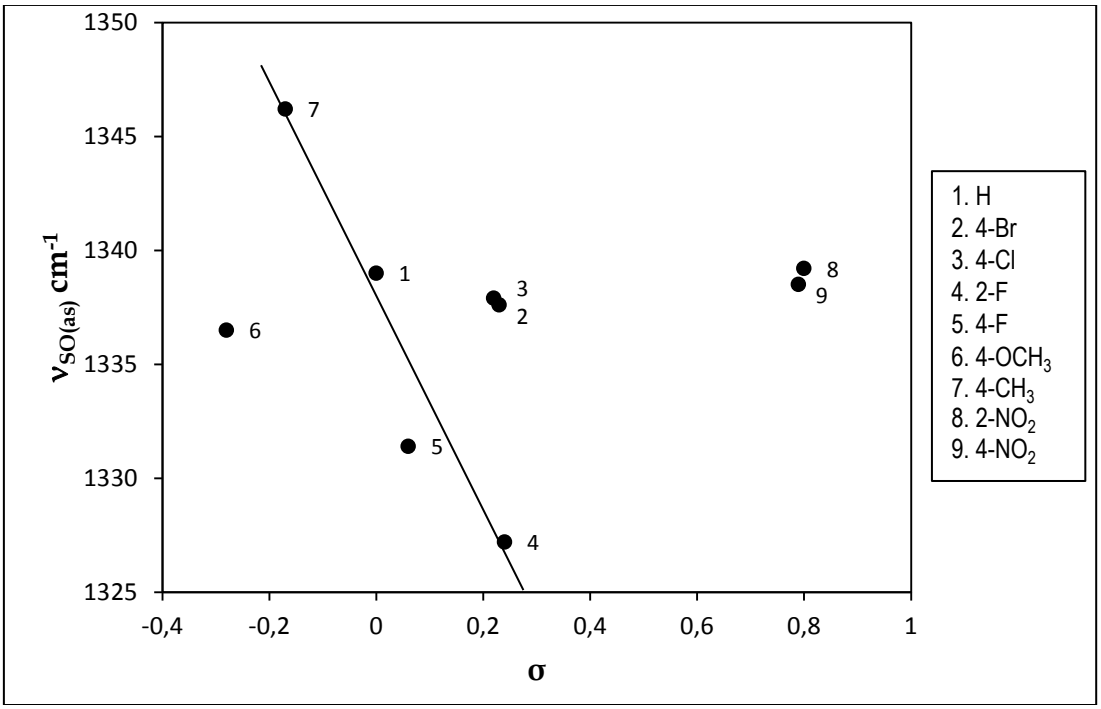


Figure 5. Single linear plot of $\nu_{SO(as)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ

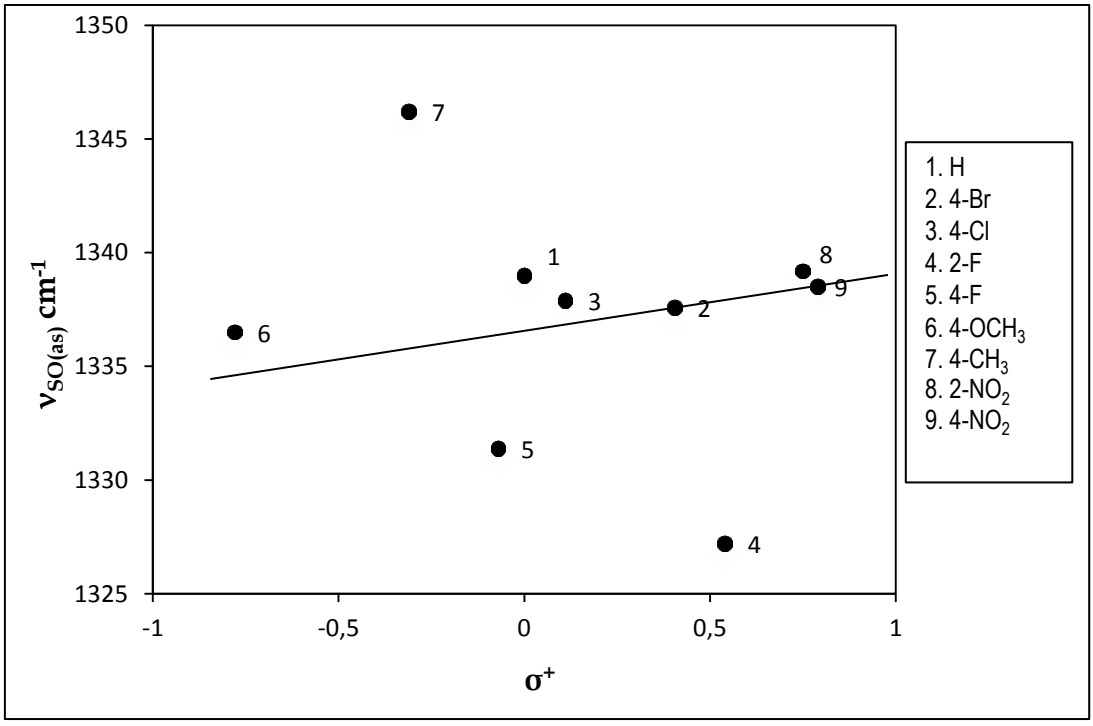


Figure 6. Single linear plot of $\nu_{SO(as)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ.

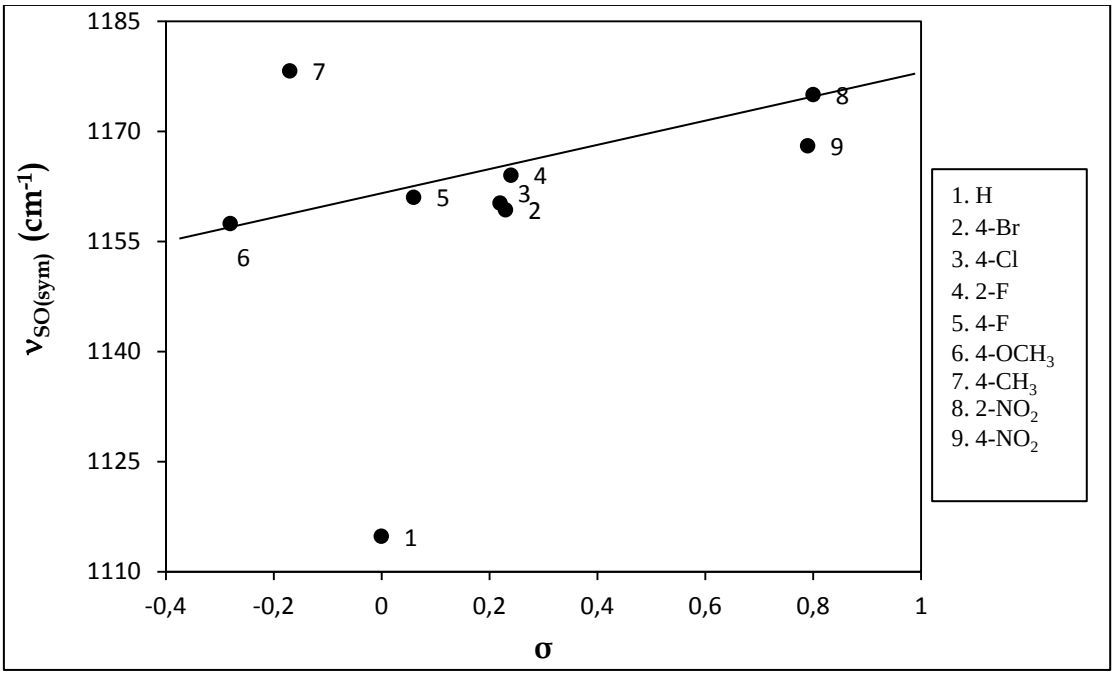


Figure 7. Single linear plot of $\nu_{SO(sym)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ

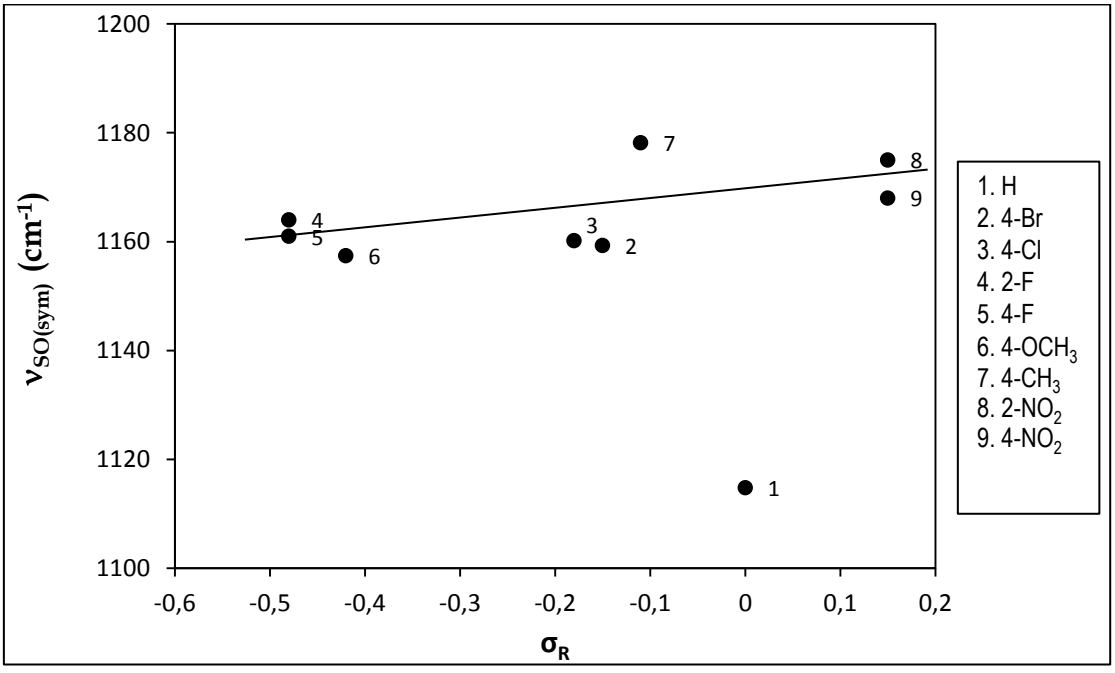


Figure 8. Single linear plot of $\nu_{SO(sym)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ

All the correlations with Hammett substituent constant viz., σ, σ^+, σ_I and *F* parameters have shown positive ρ values. This is indicates the operation of normal substituent effect substituent effect with respect to infrared frequency ($\nu_{SO(sym)}$, cm^{-1}) values of 3-(substituted phenylsulfonamido)benzoic acid compounds. The single linear plot of IR frequency ($\nu_{SO(sym)}$, cm^{-1}) values against Hammett constant σ, σ_R is shown in the following Figure 7 and Figure 8.

Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (6) and (7).

$$\nu_{SO(sym)}\ (cm^{-1}) = 1147.26(\pm12.97) + 31.334(\pm6.063)\sigma_I - 1.861(\pm0.101)\sigma_R \quad \ldots (6)$$
$$(R = 0.844,\ n = 9,\ P > 90\%)$$

$$\nu_{SO(sym)}\ (cm^{-1}) = 1148.11(\pm12.301) + 27.982(\pm3.398)F + 3.232(\pm1.335)R \quad \ldots (7)$$
$$(R = 0.944,\ n = 9,\ P > 90\%)$$

The result of statistical analysis are presented in Table-2, it is evident that the infrared frequency (ν_{CO}, cm^{-1}) values of all the 3-(substituted phenylsulfonamido)benzoic acid compounds have shown satisfactory correlation with Hammett constants σ (r = 0.905), σ_I (r = 0.903) except 4-OCH_3 substituent and Hammett constant σ_R (r = 0.905) and parameter *R* (r = 0.905) except 4-OCH_3, 4-CH_3 substituent. When these substituents that have been given exception are included in regression they reduce the correlations considerably.

The infrared frequency (ν_{CO}, cm^{-1}) values of 3-(substituted phenylsulfonamido)benzoic acid compounds have shown poor correlations (r < 0.900) with the Hammett substituent constant σ_I and R parameter. This is attributed to the weak inductive, field and resonance effects of the substituents for predicting the reactivity on the infrared frequency through resonance as per the conjugative structure as shown in Figure 2.

All the correlations with Hammett substituent constants, *F* and *R* parameters have shown negative ρ values. This is indicates the operation of reverse substituent effect with respect to infrared frequency (ν_{CO}, cm^{-1}) values of 3-(substituted phenylsulfonamido)benzoic acid compounds. The single linear plot of Infrared frequency (ν_{CO}, cm^{-1}) values against Hammett constant σ, σ_R is shown in the following Figure 9 and Figure 10.

Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (8) and (9).

$$\nu_{(CO)}\ (cm^{-1}) = 1686.68(\pm2.661) - 5.896(\pm1.347)\sigma_I - 10.653(\pm5.560)\sigma_R \quad \ldots (8)$$
$$(R = 0.967,\ n = 9,\ P > 95\%)$$

$$\nu_{(CO)}\ (cm^{-1}) = 1685.46(\pm2.679) - 3.555(\pm1.095)F - 9.896(\pm2.082)R \quad \ldots (9)$$
$$(R = 0.962,\ n = 9,\ P > 95\%)$$

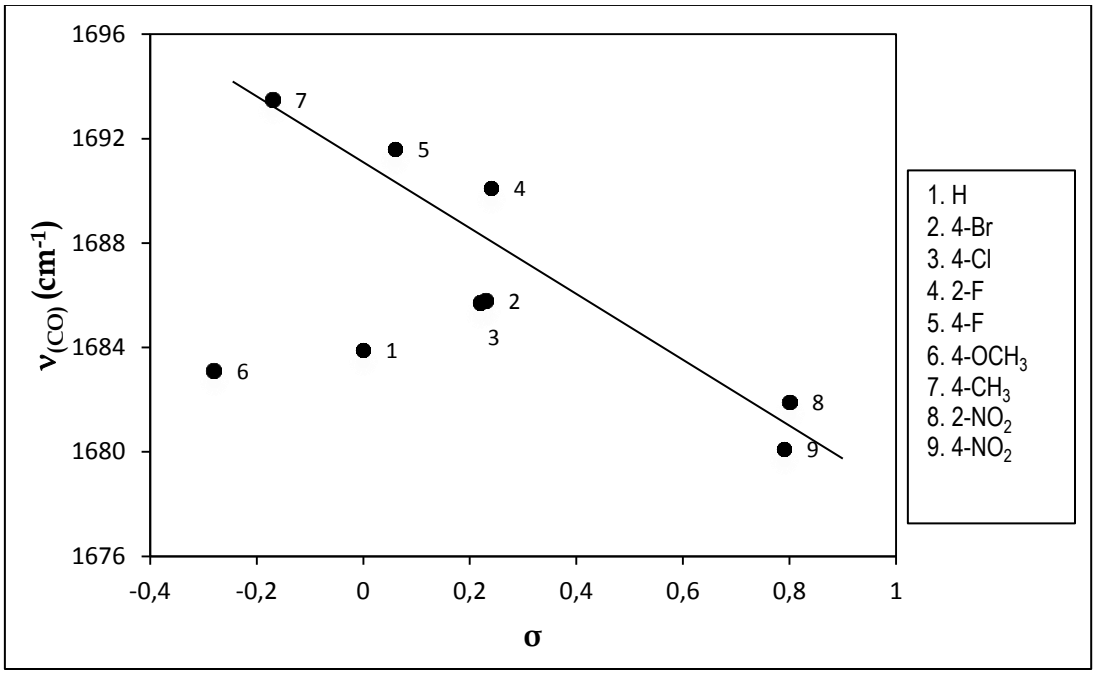


Figure 9. Single linear plot of $\nu_{(C=O)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ

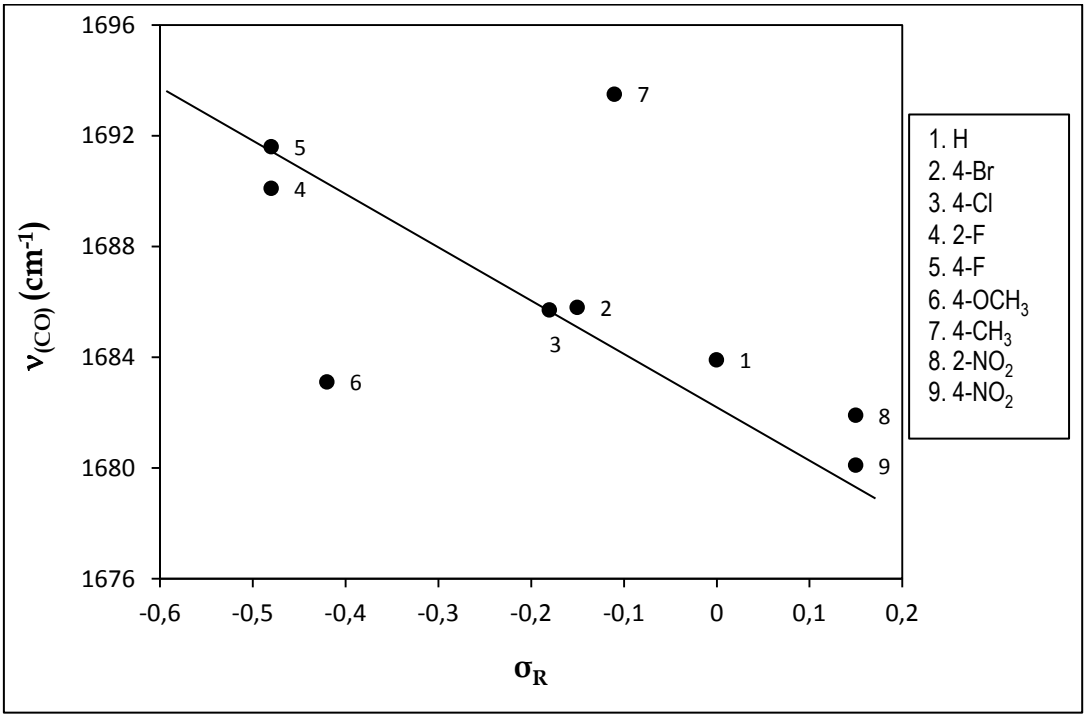


Figure 10. Single linear plot of $\nu_{(C=O)}$ (cm^{-1}) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ_R

3. 2. ^{1}H NMR correlations

The assigned NMR chemical shifts (δ, ppm) of δ_{NH} of 3-(substituted phenylsulfonamido) benzoic acids are presented in Table 1. These chemical shifts (δ, ppm) were correlated with Hammett substituent constants and Swain-Lupton's [28] parameters using single and multi- regression analysis [29-32]. In NMR spectral correlations, the Hammett equations was taken in the form of

$$\delta = \rho\sigma + \delta_o \qquad \ldots (10)$$

where δ_o is the chemical shift of unsubstituted system.

The results of statistical analyses are presented in Table 2. From Table 2, the correlation of δ_{NH} chemical shifts (δ, ppm) of 3-(substituted phenylsulfonamido)benzoic acids have shown satisfactory correlation with Hammett substituent constant σ (r = 0.965) except 4-CH_3 substituent, σ^+ (r = 0.905) except 2-F, 4-CH_3 substituent, σ_R (r = 0.958), *R* (r = 0.948) parameter except parent and 4-CH_3 substituent. The remaining Hammett substituent constants σ_I, and *F* parameter were failing in correlation. When these substituents that have been given exception are included in regression they reduce the correlations considerably. The reason for the failure correlations are already stated and associated with resonance-conjugated structure as shown in Figure 2. All the correlations with Hammett substituent constants, *F* and *R* parameters have shown positive ρ values except *F* parameter. This is indicates the operation of normal substituent effect with respect to ^{1}H NMR chemical shifts (δ_{NH}, ppm) of 3-(substituted phenylsulfonamido) benzoic acid compounds. The single linear plot of Infrared frequency (δ_{NH}, ppm) values against Hammett constant σ, σ^+ is shown in the following Figure 11 and Figure 12.

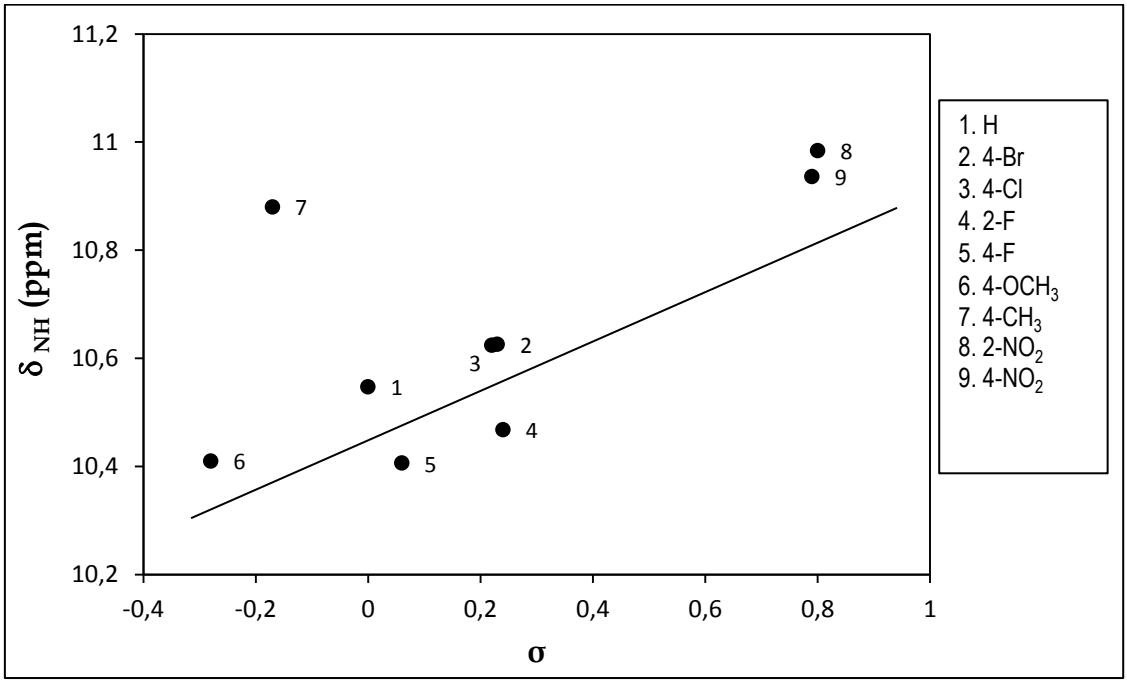


Figure 11. Single linear plot of $\delta_{(NH)}$ (ppm) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ

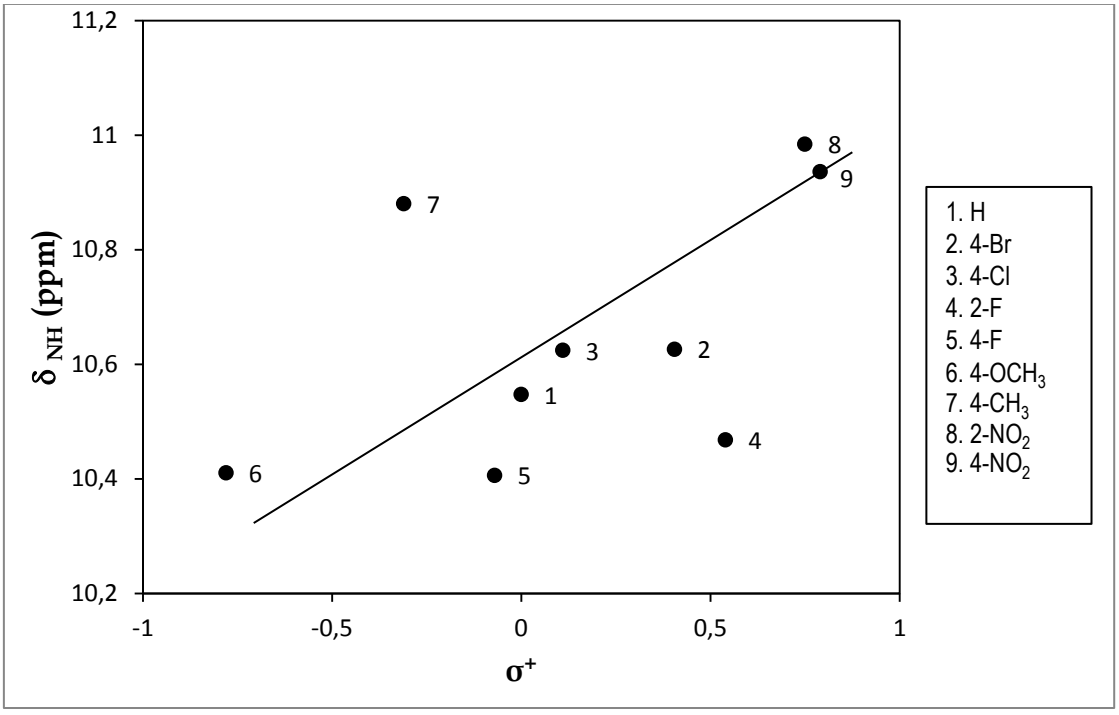


Figure 12. Single linear plot of $\delta_{(NH)}$ (ppm) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ^+

Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (11) and (12).

$$\delta_{NH}\,(ppm) = 1010.747(\pm 0.088) + 0.097(\pm 0.077)\sigma_I + 0.779(\pm 0.184)\sigma_R \quad \ldots (11)$$
$$(R = 0.986,\ n = 9,\ P > 95\%)$$

$$\delta_{NH}\,(ppm) = 1010.754(\pm 0.088) + 0.120(\pm 0.109)F + 0.666(\pm 0.168)R \quad \ldots (12)$$
$$(R = 0.985,\ n = 9,\ P > 95\%)$$

3. 3. ^{13}C NMR correlations

The assigned ^{13}C NMR chemical shifts (δ, ppm) of CO of 3-(substitutedphenyl sulfonamido)benzoic acids are presented in Table 1. These chemical shifts (δ, ppm) were correlated with Hammett substituent constants and Swain-Lupton's [25] parameters using single and multi- regression analysis [29-32].

It is evident that the ^{13}C NMR chemical shift (δ_{CO}, ppm) values of all the 3-(substituted phenylsulfonamido)benzoic acids compounds except 2-F and 4-CH_3 substituents have shown satisfactory correlations with parameter *F* (r = 0.904). All the remaining Hammett substituted constants and *R* parameter were failing in correlation. When the substituents that have been given exception are included in regression they reduced the correlation considerably.

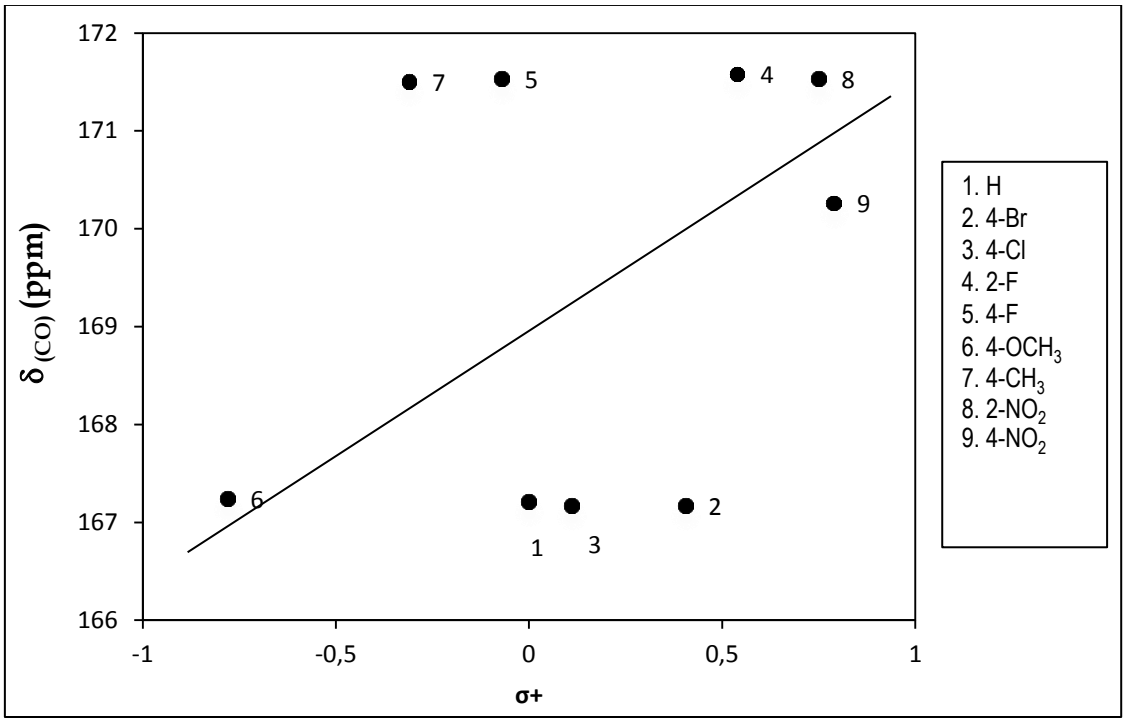


Figure 13. Single linear plot of $\delta_{(CO)}$ (ppm) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus* σ^{+}

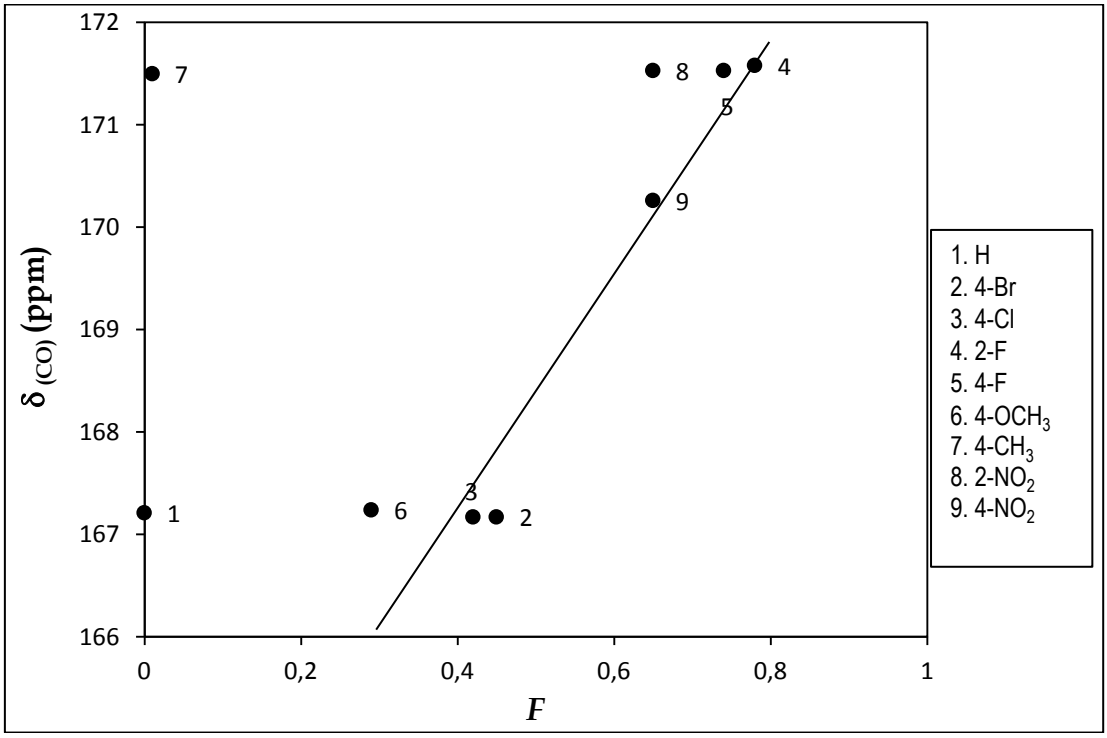


Figure 14. Single linear plot of $\delta_{(CO)}$ (ppm) of 3-(substituted phenylsulfonamido)benzoic acid compounds *versus F*

All the correlations with Hammett substituent constant viz., σ, σ^+, σ_I and *F* parameter have shown positive ρ values. It indicates the operation of normal substituent effect with respect to δ_{CO} (ppm) modes of 3-(substituted phenylsulfonamido)benzoic acids compounds.

The failure in the correlation was due to reasons stated earlier with the resonance conjugative structure as shown in Figure 2. The single linear plot of infrared frequency (δ_{CO} (ppm) values against Hammett constant σ^+, parameter *F* is shown in the following Figure 13 and Figure 14.

Most of the single regressions have shown poor correlations. Hence, the author decided to go for multi-regression analysis. The multi regression analyses have shown satisfactory correlations as shown in equations (13) and (14).

$$\delta_{CO}\,(ppm) = 168.51(\pm1.661) + 2.293(\pm3.338)\sigma_I - 0.335(\pm3.471)\sigma_R \quad \ldots (13)$$
$$(R = 0.927,\ n = 9,\ P > 90\%)$$

$$\delta_{CO}\,(ppm) = 167.97(\pm1.445) + 3.553(\pm2.749)F + 0.360(\pm0.742)R \quad \ldots (14)$$
$$(R = 0.946,\ n = 9,\ P > 90\%)$$

4. CONCLUSIONS

About nine 3-(substituted phenylsulfonamido)benzoic acids were synthesized and characteristic infrared (ν_{NH}, $\nu_{SO(as)}$, $\nu_{SO(sym)}$ and $\nu_{CO(as)}$ cm^{-1}) stretches, NMR chemical shifts (δ, ppm) of NH protons and CO carbons were assigned and correlated with Hammett substituent constants and Swain Lupton's parameters using single and multi-regression analysis. From the results of regression analysis the effect of substituents on the spectral data were studied. The infrared spectral frequencies ν_{NH} and $\nu_{SO(sym)}$ were failing in correlations. Some of the sulfonamide NH protons and carbons produced satisfactory correlations in single parameter correlations. In multi-regression analysis all spectral data gave satisfactory correlations.

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