Infrared and ^{13}C NMR spectral studies of some aryl hydrazides: Assessment of substituent effects

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ABSTRACT

A series of some aryl hydrazides have been synthesized. These hydrazides purities were analyzed by physical constants and spectral data. The assigned spectral group frequencies were correlated with Hammett substituent constants and Swain-Lupton parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the spectral group frequencies has been discussed.

Keywords: Substituted aryl benzohydrazide; IR spectra; NMR spectra; Hammett equation; Substituent constants; Correlation analysis

1. INTRODUCTION

Hydrazides are one of the derivatives of acid chloride compounds. They possess important biological activities due to their moiety contains carbonyl, N-N groups and polar substituents in aryl ring [1-8]. Spectroscopic data were utilized for the study of QSAR, QPR, QSR of organic compounds [9,10]. From these studies, the effect of substituent on the functional group have been studied. Infrared spectral data was applied for the prediction of ground state equilibrium of organic substrates such as *s-cis* and *s-trans* conformers of unsaturated carbonyl compounds, *cis-* and *trans-* geometrical isomerism of alkene, alkynes, *cis-* and *gauche-* conformers of acyl derivatives [11,12]. The ^{1}H NMR data was useful for prediction of spatial arrangement of protons such as *E* or *Z* type [13]. Recently, Kalyanasundaram et al., have studied the effect of substituents in some (*E*)-1-(4-phenoxyphenyl)-3-phenylprop-2-en-1-ones using spectral data [14]. Thirunarayanan et al., have studied the infrared and NMR spectral Hammett correlations in 4-(2-naphthyl)-5,6-dihydro-6-(substituted phenyl)-[4]*H*-1,3-oxazine-2-amines [15].

Thirunarayanan and Sekar have studied the effect of substituents by Hammett spectral correlations in benzofuranyl flavonols and pyrazoline derivatives [16,17]. Within the above view, there is no report available for the study of effect of substituents in the aryl hydrazides. Therefore the authors have taken efforts for studying the effect of substituents on the substituted benzohydrazide by infrared and ^{13}C NMR spectra.

2. EXPERIMENTAL

2. 1. General

The IR spectra (KBr, 4000-400 cm^{-1}) of all compounds have been recorded on AVATAR-300 Fourier transform spectrophotometer. The Bruker AV400 NMR spectrometer operating at 100 MHz for ^{13}C NMR spectra in CDCl3 solvent, using TMS as internal standard.

2. 2. Synthesis of substituted benzohydrazides

All substituted benzohydrazides have been synthesized and analyzed their purities by literature method [4]. The general structure of the synthesized benzohydrazide is shown in Fig. 1.
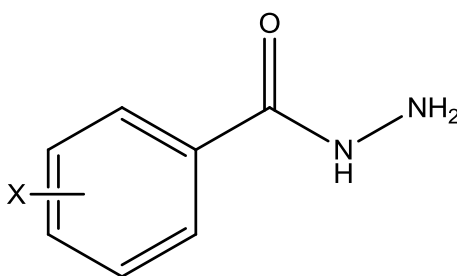
X= H, 4-NH$_2$, 3-Br, 4-Br, 4-Cl, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$

Fig. 1. The general structure of substituted benzohydrazide.

3. RESULTS AND DISCUSSION

In the present study, the authors have investigated the effect of substituents on the assigned spectral frequencies using Hammett equation with Hammett substituent constants and Swain-Lupton's [18] constants by single and multi-linear regression analysis.

3. 1. IR spectral study

In infrared spectral study, the Hammett equation is applied for prediction of effect of substituents on the carbonyl and NH stretches with Hammett substituent constants. In this correlation, the Hammett equation was taken as,

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

where ν is the frequency for the substituted system, ρ is the reaction constants in terms of intercept, σ is the substituent constants and ν_o is the frequency for the parent member of the series. The assigned carbonyl and NH stretches (ν, cm^{-1}) of all substituted benzohydrazide are presented in Table 1.

Table 1. Infrared and ^{13}C NMR spectral data of synthesized substituted benzohydrazide.

Sl. No.	X	IR (ν, cm^{-1})		^{13}C NMR (δ, ppm)	
		CO	NH	CO	C_{ipso}
1	H	1643	3342	169.34	133.75
2	4-NH$_2$	1644	3345	168.22	134.38
3	3-Br	1654	3535	168.94	133.99
4	4-Br	1658	3547	168.86	134.44
5	4-Cl	1668	3544	167.96	134.75
6	4-OCH$_3$	1638	3325	167.84	133.72
7	4-CH$_3$	1663	3376	168.34	134.17
8	3-NO$_2$	1682	3556	169.21	134.82
9	4-NO$_2$	1685	3557	169.26	134.85

The results of statistical analysis [9-17] are shown in Table 2. From the table 2, the correlation of νCO and NH stretches (ν, cm^{-1}) of hydrazide derivatives were produced satisfactory correlation coefficient. Among these correlations the σ constant gave slightly better r values. Other constants gave more or less equal r values. Similarly they produced the satisfactory correlation for multi-regression analysis with Swain-Lupton's[18] parameters. The generated multi-regression analysis equations are shown in (2-5).

$$\nu C{=}O(cm^{-1}) = 1656.22(\pm 7.227) + 26.991(\pm 14.828)\sigma_I + 44.650(\pm 17.806)\sigma_R \qquad ...(2)$$
$$(r = 0.986, n = 9, P > 95\ \%)$$
$$\nu C{=}O(cm^{-1}) = 1655.29(\pm 0.999) + 30.752(\pm 16.371)F + 29.696(\pm 14.271)R \qquad ...(3)$$
$$(r = 0.984, n = 9, P > 95\ \%)$$
$$\nu NH(cm^{-1}) = 3366.99(\pm 38.746) + 314.54(\pm 79.490)\sigma_I + 113.462(\pm 95.457)\sigma_R \qquad ...(4)$$
$$(r = 0.990, n = 9, P > 95\ \%)$$
$$\nu NH(cm^{-1}) = 3368.62(\pm 43.974) + 320.172(\pm 88.880)F + 814.699(\pm 17.498)R \qquad ...(5)$$
$$(r = 0.989, n = 9, P > 95\ \%)$$

3. 2. ^{13}C NMR Spectral study

In nuclear magnetic resonance spectra, the ^{1}H or the ^{13}C chemical shifts (δ, ppm) depend on the electronic environment of the nuclei concerned. These chemical shifts of

hydrazide have been correlated with reactivity parameters. Thus the Hammett equation was used in the form as shown in (6).

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \qquad \text{... (6)}$$

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

The assigned CO and C_{ipso} carbon chemical shifts (δ, ppm) of hydrazides have been assigned and correlated with Hammett substituent constants using single and multi-linear regression analysis [9-17]. The results of statistical analysis are shown in Table 2. From Table 2, the correlation of CO carbon chemical shifts (δ, ppm) of hydrazides with Hammett σ, σ^+, σ_R constants and R parameters were satisfactory. The Hammett σ_I constant and F parameter were fail in correlation. This is due to the inability of prediction of the effect of substituents on the carbonyl chemical shifts and is associated with the resonance-conjugative structure as shown in Figure 2.
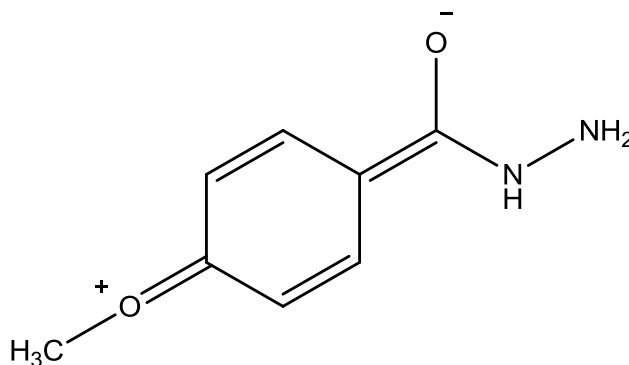

Fig. 2. The resonance-conjugative structure.

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

Frequency	Constant	r	I	ρ	s	n	Correlated derivatives
νCO (cm^{-1})	σ	0.981	1655.41	29.024	10.34	9	H, 4-NH$_2$, 3-Br, 4-Br, 4-Cl, 4-OCH$_3$, 4-CH$_3$, 2-NO$_2$, 4-NO$_2$
	σ^+	0.907	1659.34	18.116	11.74		
	σ_I	0.906	1644.64	43.678	12.04		
	σ_R	0.907	1667.27	59.222	11.34		
	F	0.907	1643.74	47.092	12.54		
	R	0.917	1668.19	42.560	12.05		

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νNH (cm⁻¹)	σ	0.985	3431.67	193.412	59.39	9	H, 4-NH₂, 3-Br, 4-Br, 4-Cl, 4-OCH₃, 4-CH₃, 2-NO₂, 4-NO₂
	σ^+	0.908	3457.83	129.127	61.41		
	σ_I	0.908	3337.52	357.142	54.33		
	σ_R	0.905	3496.07	283.759	92.86		
	F	0.908	3336.84	365.132	36.51		
	R	0.905	3502.88	215.636	92.32		
δCO (ppm)	σ	0.965	168.55	0.812	0.46	9	H, 4-NH₂, 3-Br, 4-Br, 4-Cl, 4-OCH₃, 4-CH₃, 2-NO₂, 4-NO₂
	σ^+	0.971	168.66	0.591	0.43		
	σ_I	0.821	168.43	0.685	0.59		
	σ_R	0.968	168.94	2.135	0.36		
	F	0.732	168.91	0.741	0.58		
	R	0.977	168.97	1.507	0.40		
δC$_{ipso}$ (ppm)	σ	0.956	134.24	0.523	0.38	9	H, 4-NH₂, 3-Br, 4-Br, 4-Cl, 4-OCH₃, 4-CH₃, 2-NO₂, 4-NO₂
	σ^+	0.948	134.31	0.303	0.41		
	σ_I	0.967	133.93	1.125	0.34		
	σ_R	0.944	134.43	0.936	0.42		
	F	0.965	133.93	1.136	0.35		
	R	0.904	134.44	0.610	0.43		

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

The correlation of C$_{ipso}$ carbon chemical shifts (δ, ppm) of hydrazides gave satisfactory correlation with Hammett substituent constants [9-17] and F and R parameters [18]. Among these correlations, the Hammett σ_I constants gave slightly better r values. The other correlations are more or less uniform. The multi-linear correlation of CO and C$_{ipso}$ carbon chemical shifts (δ, ppm) of hydrazides were produced satisfactorily correlation coefficients.

The generated correlation equations are shown in (7-10).

$$\nu C=O(cm^{-1}) = 169.00(\pm0.298) + 1.147(\pm0.059)\sigma_I + 2.218(\pm0.713)\sigma_R \quad ...(7)$$
$$(r = 0.980, n = 9, P > 95\%)$$
$$\nu C=O(cm^{-1}) = 169.02(\pm0.341) + 0.117(\pm0.069)F + 1.555(\pm0.605)R \quad ...(8)$$
$$(r = 0.975, n = 9, P > 95\%)$$

$$\nu NH(cm^{-1}) = 134.03(\pm 0.269) + 0.986(\pm 0.055)\sigma_I + 0.369(\pm 0.066)\sigma_R \qquad ...(9)$$
$$(r = 0.969, n = 9, P > 95\ \%)$$
$$\nu NH(cm^{-1}) = 134.00(\pm 0.297) + 1.014(\pm 0.601)F + 0.174(\pm 0.051)R \qquad ...(10)$$
$$(r = 0.966, n = 9, P > 95\ \%)$$

4. CONCLUSIONS

A series of some aryl hydrazides have been synthesized and recorded their infrared and ^{13}C NMR spectra. The assigned spectral group frequencies were correlated with Hammett substituent constants and Swain-Lupton parameters using single and multi-linear regression analysis. In infrared spectral correlations, all regressions gave satisfactory *r* values. In ^{13}C NMR spectral correlations, the carbonyl carbon chemical shifts correlated satisfactorily with Hammett σ, σ^+, σ_R constants and R parameters. The correlation of C$_{ipso}$ carbon chemical shifts (δ, ppm) of hydrazides gave satisfactory correlation with Hammett substituent constants and F and R parameters. In multi-regression analysis all spectral data of the hydrazides gave satisfactory correlations.

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