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Synthesis and spectral correlation studies of some (*E*)-N′-1-(substituted benzylidene) benzohydrazides

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ABSTRACT

About ten substituted (*E*)-*N'*-1-(substituted benzylidene) benzohydrazides have been synthesized. They are characterized by their analytical, ultraviolet, infrared and NMR spectral data. The effects of substituent on these data have been studied using Hammett equation.

***Keywords*:** (*E*)-*N'*-1-(substituted benzylidene) benzohydrazides, UV, IR and NMR spectra and Correlations

1. INTRODUCTION

The chemistry of heterocyclic compounds has been an interesting field of study for a long time. Hydrazone compounds containing two nitrogen atoms and one carbonyl group linked by phenyl rings. Aryl hydrazones has been most suitably synthesized by the result of aryl hydrazines with carbonyl compounds. Hydrazones taking an azomethine –NHN=CH– proton add up to an essential class of compounds for new drug discovery. Therefore, many

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researchers [1,2] has synthesized these compounds as well as their metal complexes as target structures their biological activities are evaluated.

Hydrazide-hydrazones compounds are reactive intermediates and also very effective organic compounds in their functional groups. By the bimolecular condensation of carbonyl compound with an aryl or alkyl hydrazine the resulting compound is aryl or alkyl hydrazones. Due to their artificial ease and active pharmacophore group, *i.e.*, the C=N moiety, hydrazones are establish their catalytic activities.

By the heating of appropriate substituted hydrazides or hydrazines with substituted aldehydes and ketones in the solvents like butanol, methanol, ethanol, glacial acetic acid, ethanol-glacial acetic acid and tetrahydrofuran to form an azomethine –NHN=CH– proton containing hydrazones. They are differing from their family like imines and oximes by the presence of interlinked nitrogen atoms [3].

Hydrazones also known as Schiff base family, they have azomethine –NHN=CH– protons and they are considered as the essential class of compounds for the enlargement of new drugs [4]. The metal complexes of hydrazone compounds show major part in treatment of different diseases. The improvement of a more efficient and convenient method[5], for the synthesis of 1-substituted tetrazoles under solvent-free conditions still remains an active research area.

For synthetic organic chemistry solid acid catalysts [6-10], are using new technology. Among various silica-based heterogeneous catalysts, silica sulfuric acid has advantages of not expensive, yield of preparation and recyclability. It is insoluble in all organic solvents.

In our human body free radicals and essential elements are may act as important roles in the biological evolution and origin of life, associated by their positive effects in many types of organisms [11]. However, cellular components are directly attacked by extremely unstable free radicals, containing one or more unpaired electrons. These are responsible for many diseases including cancer, ischaemia and reperfusion injury in many tissues, the damage of central nervous system and AIDS [12].

This study is useful for ground state equilibration behavior of carbonyl and vinyl compounds through infrared spectra [13-17]. The spatial arrangement of vinyl and heterocyclic ring protons were confirmed by proton NMR spectra [18-21]. Recently Vijayakumar et al., have studied the spectral correlation study of some substituted (*E*)-2-benzylidene hydrazinecarbothio amides and observed satisfactory and good correlation coefficients in Hammett parameters of single and multi-correlations.

Within the above view, some informations only available in literature in the past for synthesis, spectral correlation analysis of the title compounds. Therefore the authors have taken efforts for the synthesis of (*E*)-*N'*-1-(substituted benzylidene) benzohydrazides to study the quantitative structure activity relationships by spectral correlation through Hammett equation with their Ultra-Violet, Infra-Red and NMR spectral data.

2. EXPERIMENTAL

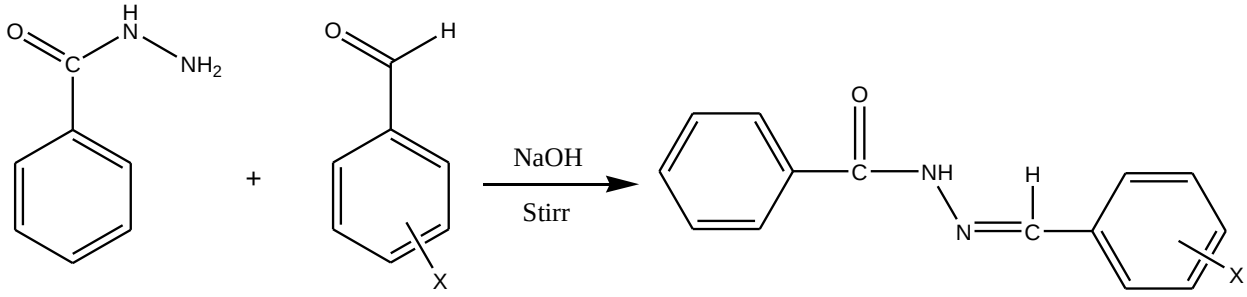
2. 1. Materials and Systematic methods

All chemicals were used and purchased from Sigma-Aldrich chemical company Bangalore. All synthesized hydrazone compounds melting points are observed from uncorrected Suntex melting point apparatus using open glass capillaries.

The above hydrazones for Ultra violet spectra recorded using ELICO-double beam BL222 Bio-Spectrophotometer. Infrared spectra (KBr, 4000-400 cm^{-1}) have been recorded on AVATAR-300 FT-IR spectrophotometer. BRUKER-400MHz NMR spectrometers has been operated for recording ^{1}H and ^{13}C spectra in $CDCl_3$ solvent using internal standard as TMS.

2. 2. General procedure for synthesis of (*E*)-*N'*-1-(substituted benzylidene) benzohydrazides

An appropriate molar concentration mixture of benzhydrazide (100 mmol) and *ortho, meta* and *para* substituted benzaldehydes (100 mmol) and aqueous solution of sodium hydroxide (200 ml 0.5 M) with absolute ethanol (**Scheme 1**). The reactants are vigorously stirred at normal temperature for 30 minutes [13]. After complete renovation of the benzaldehydes as examined by TLC, the mixture was may allow to 20 minutes for undisturbed condition. By the filtration method is used to removal of unreacted reagents. The filtrate was cleaned with distilled water and recrystallized from absolute ethanol, dried well and kept in a desiccator.



X = H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2

Scheme 1

The synthesized (*E*)-*N'*-(1-(substituted benzylidene) benzohydrazides have been characterized by their physical constants, elemental analysis and spectral data. The physical constants, analytical and micro analysis data of these (*E*)-*N'*-(1-(substituted benzylidene) benzohydrazides are shown in **Table 1**. The spectral data of synthesized substituted (*E*)-*N'*-(1-substituted benzylidene) benzohydrazides are shown in **Table 2**.

Table 1. Physical constants of substituted (*E*)-*N'*-(1-substituted benzylidene) benzohydrazides.

Entry	X	MF	MW	Yield (%)	Mp (ºC)	Found (Calcd.) (%)		
						C	H	N
1	H	$C_{14}H_{12}N_2O$	224	92	165-166	74.45 (74.98)	5.28 (5.39)	12.26 (12.49)

2	3-Br	$C_{14}H_{11}BrN_2O$	303	90	138-139	55.26 (55.47)	3.42 (3.66)	9.10 (9.24)
3	2-Cl	$C_{14}H_{11}ClN_2O$	258	89	141-142	64.86 (65.00)	4.14 (4.29)	10.53 (10.83)
4	4-Cl	$C_{14}H_{11}ClN_2O$	258	91	147-148	64.98 (65.00)	4.18 (4.29)	10.68 (10.83)
5	4-F	$C_{14}H_{11}FN_2O$	242	91	149-150	69.24 (69.41)	4.44 (4.58)	11.26 (11.56)
6	3-OH	$C_{14}H_{12}N_2O_2$	240	93	163-164	69.28 (69.99)	4.95 (5.03)	13.14 (13.32)
7	4-OH	$C_{14}H_{12}N_2O_2$	240	94	161-162	69.22 (69.99)	4.98 (5.03)	13.22 (13.32)
8	4-CH_3	$C_{15}H_{14}N_2O$	238	89	120-121	75.09 (75.61)	5.88 (5.92)	11.24 (11.76)
9	2-NO_2	$C_{14}H_{11}N_3O_3$	269	93	173-174	62.15 (62.45)	4.02 (4.12)	15.48 (15.61)
10	3-NO_2	$C_{14}H_{11}N_3O_3$	269	90	165-166	62.05 (62.45)	4.06 (4.12)	15.38 (15.61)

Table 2. The ultraviolet absorption maxima ($\lambda_{max,}$ nm), infrared absorptions (υ, cm^{-1}) and NMR chemical shifts (δ ppm) spectral data of substituted (*E*)-*N'*-(1-substituted benzylidene) benzohydrazide compounds.

Entry	X	UV (nm) λ_{max}	IR ν (cm^{-1})			^{1}H NMR (δ, ppm)		^{13}C NMR (δ, ppm)	
			C=O	C=N	N-H	N-H	C-H	C=O	C=N
1	H	323.0	1666.50	1539.20	3284.77	9.225	8.329	163.28	128.78
2	3-Br	332.0	1651.07	1539.20	3398.57	9.426	8.313	164.65	130.28
3	2-Cl	290.0	1647.21	1546.91	3188.33	9.304	8.318	166.74	132.09
4	4-Cl	323.0	1662.64	1543.05	3284.77	9.482	8.319	164.66	132.11
5	4-F	323.0	1649.14	1550.77	3201.83	9.146	8.317	162.98	132.46
6	3-OH	309.0	1645.28	1544.98	3197.98	9.331	8.518	162.86	129.87
7	4-OH	323.0	1647.21	1560.41	3197.98	9.234	7.755	164.32	131.98
8	4-CH_3	308.0	1647.21	1550.77	3197.88	9.285	8.291	165.40	143.53
9	2-NO_2	323.0	1647.21	1553.76	3182.55	9.698	8.722	163.06	432.69
10	3-NO_2	323.0	1641.42	1527.62	3383.14	9.322	8.207	164.56	133.46

3. RESULTS AND DISCUSSION

3. 1. Spectral linearity

In the current study the spectral linearity of synthesized (*E*)-*N'*-(1-benzylidene) benzohydrazides has been studied by evaluating the substituent effects. The observed spectral data for the benzohydrazides, UV λ max (nm), infrared νC=O, νC=N, νN-H, the proton chemical shifts δ (ppm) of N-H, C-H and carbon chemical shifts of C=O and C=N are correlated with various substituent constants [14-17, 23].

3. 2. UV spectral study

The measured absorption maxima (λ_{max} nm) values of the synthesized (*E*)-*N'*-(1-benzylidene) benzohydrazide compounds have been recorded and presented in **Table 2.** These data are correlated with Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analysis [14-17, 23]. Hammett equation employed for the correlation analysis, involving the absorption maxima is as shown below in equation (1).

$$\lambda = \rho\sigma + \lambda o \qquad \ldots (1)$$

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

From the **Table 3**, it is evident that the UV absorption maximum (λ_{max} nm) values of all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazide compounds, have shown poor correlations ($r < 0.900$) with Hammett substituent constants and *F* and *R* parameters. This is attributed to the weak polar, inductive, field and resonance effects of substituents for predicting the reactivity on the UV absorption through resonance as per the conjugative structure as shown in **Figure 1.**

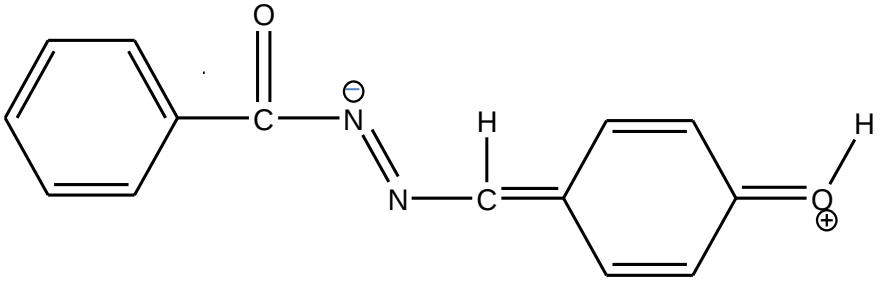


Figure 1. Resonance conjugative structure.

All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to UV absorption maximum (λ_{max} nm) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazide compounds. All the single parameter correlations failed for the UV absorption maximum (λ_{max} nm) values with Hammett constants and *F* and *R* parameter, it is decided to go for multi regression analysis with Swain-Lupton's [23] parameters. While pursuing the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (2 and 3).

Table 3. The results of statistical analysis of ultraviolet absorption maxima (λ_{max} nm), infrared absoptions (υ, cm^{-1}) and NMR chemical shifts (δ ppm) of substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides with Hammett σ, σ^+, σ_I, σ_R and *F* and *R* parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max}	σ	0.787	316.26	7.790	12.42	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.768	317.61	1.977	12.74	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.695	313.97	9.954	12.53	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.825	319.51	10.743	12.53	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.767	312.91	12.054	12.38	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.781	319.45	5.656	12.53	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
νC=O	σ	0.813	1651.26	-4.187	8.19	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.842	1650.50	-0.378	8.35	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.831	1655.06	-12.241	7.72	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.789	1650.90	2.457	8.33	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.846	1655.85	-13.514	7.53	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.822	1651.79	4.195	8.13	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
νC=N	σ	0.905	1547.95	-12.440	8.37	9	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 3-NO_2
	σ^+	0.907	1546.02	-8.371	8.27	9	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 3-NO_2
	σ_I	0.819	1548.29	-7.022	9.53	9	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 3-NO_2
	σ_R	0.905	1542.11	-20.991	8.30	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2

	F	0.798	1546.69	-2.577	9.67	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.835	1543.19	-7.945	9.00	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
νN-H	σ	0.957	3233.99	96.603	78.60	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.904	3249.06	63.979	78.28	8	H, 3-Br, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 3-NO_2
	σ_I	0.822	3223.40	75.859	85.06	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.846	3278.11	155.801	78.96	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.811	3236.30	38.981	86.68	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.849	3276.05	78.046	79.79	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
δN-H	σ	0.906	9.292	0.288	0.12	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.905	9.339	0.144	0.14	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.857	9.236	0.290	0.14	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.905	9.411	0.393	0.13	8	3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2
	F	0.822	9.274	0.177	0.15	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.837	9.389	0.142	0.15	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
δC-H	σ	0.857	8.240	0.370	0.21	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.859	8.300	0.207	0.22	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.823	8.222	0.232	0.25	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.841	8.384	0.446	0.23	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2

	F	0.871	8.240	0.171	0.25	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.817	8.339	0.097	0.25	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
δCO	σ	0.805	164.28	-0.192	1.31	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.829	164.23	0.455	1.28	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.840	164.33	-0.217	1.31	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.830	164.28	0.005	1.31	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.817	164.59	-0.876	1.29	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.829	164.51	0.845	1.25	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
δC=N	σ	0.800	135.58	147.434	82.31	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ^+	0.834	159.65	72.157	90.77	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_I	0.832	107.19	148.479	93.04	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	σ_R	0.854	198.49	211.665	87.06	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	F	0.831	111.58	128.833	94.63	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2
	R	0.837	188.28	82.174	93.53	10	H, 3-Br, 2-Cl, 4-Cl, 4-F, 3-OH, 4-OH, 4-CH_3, 2-NO_2, 3-NO_2

r = Correlation co-efficient; ρ = slope; I = Intercept; s = Standard deviation;
n = Number of substituents.

$$\lambda \text{ max (nm)} = 316.05\ (\pm 9.073) + 8.581\ (\pm 18.216)\sigma_I + 9.241\ (\pm 19.770)\ \sigma_R \quad \ldots (2)$$
$$(r = 0.934,\ n = 10,\ P > 90\%)$$

$$\lambda \text{ max (nm)} = 314.78\ (\pm 8.792) + 11.367\ (\pm 17.267)\ F + 5.129\ (\pm 7.149)\ R \quad \ldots (3)$$
$$(r = 0.931,\ n = 10,\ P > 90\%)$$

3. 3. IR spectral study

The assigned infrared frequencies (cm^{-1}) of νC=O, νC=N, νN-H of substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides are presented in **Table 2**.

The measured infrared frequency values are correlated [14-17, 22] with Hammett substituent constants and *F* and *R* parameters using single and multi-linear regression analysis. Hammett equation employed for the correlation analysis, involving the absorption maxima is as shown below in equation (4).

$$\upsilon = \rho\sigma + \upsilon_o \quad \ldots(4)$$

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

3. 4. IR Spectral Correlation of υC=O (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υC=O (cm^{-1}) values of all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have shown poor correlations ($r < 0.900$) with Hammett substituent constants and *F* and *R* parameters. This is attributed to the weak polar, inductive, field and resonance effects of substituents for predicting the reactivity on the IR frequency υC=O (cm^{-1}) through resonance as per the conjugative structure as shown in **Figure 1.**

All the correlations have shown negative ρ values except σ_R constant and R parameter. This indicates the operation of reverse substituent effect with respect to IR frequency υC=O (cm^{-1}) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

3. 5. IR Spectral Correlation of υC=N (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υC=N (cm^{-1}) values of all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have shown satisfactory correlations with Hammett substituent constants σ ($r = 0.905$), σ^+ ($r = 0.907$) and σ_R ($r = 0.905$). However, the IR frequency υC=N (cm^{-1}) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds, have shown poor correlation ($r < 0.900$) with remaining Hammett substituent constant σ_I and *F* and *R* parameters. This is attributed to the weak inductive, field and resonance effects of substituents for predicting the reactivity on the IR frequency υC=N (cm^{-1}) through resonance as per the conjugative structure as shown in **Figure 1.** All the correlations have shown negative ρ values. This indicates the operation of reverse substituent effect with respect to IR frequency υC=N (cm^{-1}) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

3. 6. IR Spectral Correlation of υ N-H (cm^{-1})

From the **Table 3**, it is evident that the IR frequency υN-H (cm^{-1}) values of all substituted (*E*)-*N'*-(1-benzylidene)benzohydrazides compounds have satisfactory correlations with Hammett substituent constants σ ($r = 0.905$) and σ^+ ($r = 0.907$). However, the IR frequency υN-H(cm^{-1}) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds, have shown poor correlation ($r < 0.900$) with remaining Hammett substituent constant σ_I, σ_R and *F* and *R* parameters. This is attributed to the weak inductive, field and resonance effects of substituents for predicting the reactivity on the IR frequency υN-H (cm^{-1}) through

resonance as per the conjugative structure as shown in **Figure 1**. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency υN-H (cm^{-1}) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

Some of the single parameter correlations failed for the IR frequency υC=O, υC=N and υN-H, (cm^{-1}) values with Hammett constants and *F* and *R* parameter, it is decided to go for multi regression analysis with Swain-Lupton's [24] parameters. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (5 to 10).

$$\nu CO\ (cm^{-1}) = 1656.12(\pm5.622) - 12.943(\pm11.287)\sigma_I + 4.723(\pm12.250)\ \sigma_R \quad \ldots(5)$$
$$(r = 0.934,\ n = 10,\ P > 90\%)$$

$$\nu CO\ (cm^{-1}) = 1657.62(\pm5.209) - 14.164(\pm10.231)F + 4.852(\pm6.020)R \quad \ldots(6)$$
$$(r = 0.955,\ n = 11,\ P > 95\%)$$

$$\nu C{=}N\ (cm^{-1}) = 1543.73(\pm6.058) - 4.006(\pm12.162)\sigma_I - 20.290(\pm13.199)\ \sigma_R \quad \ldots(7)$$
$$(r = 0.957\ n = 10,\ P > 95\%)$$

$$\nu C{=}N\ (cm^{-1}) = 1543.82(\pm6.503) - 1.522(\pm12.771)F - 7.875(\pm7.514)\ R \quad \ldots(8)$$
$$(r = 0.937,\ n = 10,\ P > 90\%)$$

$$\nu N\text{-}H\ (cm^{-1}) = 3256.27(\pm57.154) + 58.109(\pm114.743)\sigma_I + 146.327(\pm124.532)\ \sigma_R \quad \ldots(9)$$
$$(r = 0.945,\ n = 10,\ P > 90\%)$$

$$\nu N\text{-}H\ (cm^{-1}) = 3264.24(\pm57.408) + 28.703(\pm112.745)F + 76.715(\pm66.336)\ R \quad \ldots(10)$$
$$(r = 0.941,\ n = 10,\ P > 90\%)$$

3. 7. NMR spectral study

In nuclear magnetic resonance spectra, the proton and the ^{13}C chemical shifts (δ) depends on the electronic environment of the nuclei concerned. The assigned chemical shifts (ppm) have been correlated with reactivity parameters using Hammett equation in the form of

$$\delta = \rho\sigma + \delta_o \quad \ldots(11)$$

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

3. 8. ^{1}H NMR Spectral Correlation

3. 8. 1. ^{1}H NMR Spectral Correlations of N-H (ppm)

From the **Table 3**, the assigned N-H chemical shifts (δ ppm) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have shown satisfactory correlations with Hammett substituent constants σ (r = 0.900), σ^+ (r = 0.906) and σ_R (r = 0.905). However, (δ ppm) ^{1}H NMR values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds, have shown poor correlations (r < 0.900) with remaining Hammett substituent constant σ_I and *F* and *R* parameters. This is attributed to the weak, inductive, field resonance effects of substituents.

The substituents effect for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure as shown in **Figure 1.**

All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-*N'*-(1-benzylidene)benzohydrazides compounds.

3. 8. 2. ^{1}H NMR Spectral Correlations of C-H (ppm)

From the **Table 3**, the assigned –C-H chemical shifts (δ ppm) values of (*E*)-*N'*-(1-benzylidene)benzohydrazides compounds have shown poor correlations (r < 0.900) with Hammett substituent constants and *F* and *R* parameter. This is attributed to the weak, polar, inductive, field and resonance effects of substituents. The substituents effect for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure as shown in **Figure 1.**

All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in some substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

Some of the single parameter correlations analyses failed for the –C-H chemical shifts (δ ppm) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds with Hammett substituent constants and *F* and *R* parameter, it is decided to go for multi regression analysis with Swain-Lupton's[24] parameters. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (12 to 15).

$$\delta\text{N-H (ppm)} = 9.315(\pm0.090) + 0.238(\pm0.182)\sigma_I + 0.351(\pm0.197)\sigma_R \quad \ldots(12)$$
$$(r = 0.967,\ n = 10,\ P > 95\%)$$

$$\delta\text{N-H (ppm)} = 9.323(\pm0.106) + 0.159(\pm0.209)\ F + 0.135(\pm0.123)R \quad \ldots(13)$$
$$(r = 0.949,\ n = 10,\ P > 90\%)$$

$$\delta\text{C-H (ppm)} = 8.315(\pm0.169) + 0.170(\pm0.340)\sigma_I + 0.416(\pm0.369)\sigma_R \quad \ldots(14)$$
$$(r = 0.944,\ n = 10,\ P > 90\%)$$

$$\delta\text{C-H (ppm)} = 8.273(\pm0.181) + 0.159(\pm0.355)F + 0.089(\pm0.209)R \quad \ldots(15)$$
$$(r = 0.935,\ n = 10,\ P > 90\%)$$

3. 8. 3. ^{13}C NMR Spectral Correlation

3. 8. 3. 1. ^{13}C NMR Spectral Correlations of C=O (ppm)

From the Table-3, the assigned C=O chemical shifts (δ ppm) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have shown poor correlations (r < 0.900) with Hammett substituent constants and *F* and *R* parameter. This is attributed to the weak, polar, inductive, field and resonance effects of substituents. The substituents effect for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure as shown in **Figure 1.** Some of the correlations have shown positive ρ values except σ^{+}, σ_R and *R* parameter. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

3. 8. 3. 2. ^{13}C NMR Spectral Correlations of C=N (ppm)

From the Table 3, the assigned C=N chemical shifts (δ ppm) values of (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have shown poor correlations (r < 0.900) with Hammett substituent constants and *F* and *R* parameter. This is attributed to the weak, polar, inductive, field and resonance effects of substituents. The substituents effect for predicting the reactivity on the chemical shifts through resonance as per the conjugative structure as shown in **Figure 1.**

All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to NMR spectral values (ppm) values in all substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds.

All the single parameter correlations analyses have shown with Hammett substituent constants and *F* and *R* parameter, it is decided to go for multi regression analysis with Swain-Lupton's paameters [24]. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (16 to 19).

$$\delta C{=}O\ (ppm) = 164.883(\pm 0.965) - 0.254(\pm 1.938)\sigma_I + 0.249(\pm 2.103)\ \sigma_R \quad \ldots(16)$$
$$(r = 0.908,\ n = 10,\ P > 90\%)$$

$$\delta C{=}O\ (ppm) = 164.923(\pm 0.889) - 0.995(\pm 1.746)F + 0.891(\pm 1.027)\ R \quad \ldots(17)$$
$$(r = 0.935,\ n = 10,\ P > 90\%)$$

$$\delta C{=}N\ (ppm) = 150.007(\pm 59.877) + 120.145(\pm 120.209)\sigma_I + 190.631(\pm 130.464)\sigma_R \quad \ldots(18)$$
$$(r = 0.958,\ n = 10,\ P > 95\%)$$

$$\delta C{=}N\ (ppm) = 139.502(\pm 63.635) + 118.561(\pm 124.974)F + 76.675(\pm 73.531)R \quad \ldots(19)$$
$$(r = 0.948,\ n = 10,\ P > 90\%)$$

4. CONCLUSIONS

A series of ten numbers of substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have been synthesized by condensation of benzohydrazide and substituted acetophenones. These synthesized substituted (*E*)-*N'*-(1-benzylidene) benzohydrazides compounds have been characterized by their physical constants, spectral data. The UV, IR, NMR spectral data of these aryl hydrazides has been correlated with Hammett substituent constants and *F* and *R* parameters. From the results of statistical analyses the effects of substituent on the spectral data have been studied. IR and NMR spectral correlations produced more number of satisfactory correlations. But UV spectral values give poor correlations with all Hammett substituents constants and Swain-Lupton's parameters. However, all the multi-regression analyses have shown satisfactory correlations.

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