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Synthesis and LFER study of some substituted hydrazones

R. Vijayakumar[1], M. Rajarajan[2], R. Senbagam[2], S. Balaji[2], V. Manikandan[2], G. Vanangamudi[2] and G. Thirunarayanan[3,*]

[1]Department of Chemistry, Annai College of Engineering and Technology, Kovilacheri - 612 503 Kumbakonam, India

[2]PG & Research Department of Chemistry, Government Arts College, C-Mutlur - 608 102, Chidambaram, India

[3]Department of Chemistry, Annamalai University, Annamalainagar - 608 002, India

*E-mail address: drgtnarayanan@gmail.com , thirunarayanan.g.10313@annamalaiuniversity.ac.in

ABSTRACT

A series containing ten substituted hydrazones have been synthesized by condensation between semicarbazide and various substituted benzaldehydes. The hydrazones were confirmed by their physical constants and UV, IR, ^{1}H NMR and ^{13}C NMR spectral data. This UV, IR, ^{1}H NMR and ^{13}C NMR spectral data have been used for LFER studied with Hammett constants and Swain-Lupton's parameters.

***Keywords*:** Synthesis, LFER study, Hydrazones and substituent effect

1. INTRODUCTION

The chemistry of hydrazones has gained intensive attention among the researchers during the world owing to their biological and industrial applications. Hydrazones are characterized by the presence of triatomic -C=N-N- group. These two nitrogen atoms are connected by a single bond. Among these two nitrogen atoms, one nitrogen atom was

connected with a carbon atom by double bond. Another nitrogen atom was conjugated with the double bond by using its lone pair electron.

Both the two nitrogen atoms of the hydrazone group are nucleophilic in nature, although the amino type nitrogen is more reactive. But the carbon atom of hydrazone group has possessed both electrophilic and nucleophilic character [1].

Hydrazone –NH─N=CH─ functional group is ubiquitous in various fields ranging from organic synthesis, [2] medicinal chemistry, [3] Chagas disease [4] and used as a metal frameworks, [5] dye [6] dynamic combinatorial chemistry (DCC), [7] and hole-transporting materials, [8,9]. Some hydrazone compounds have been established as chromogenic reagents in transition-metal ions and metal extracts [10-13]. The hydrazone compound functional group is a great efficient pharmacophore that is widely used in pesticide design. Hydrazones compounds demonstrated antiparasitic [14], antidepressant [15], cardioprotective [16], anti-HIV [17], anticancer [18] and antioxidant [19].

In the present study the correlation of structure of compounds of the type (Fig-1) containing a substituent (R) and a side chain (Y), with their reactivity was usually, relating the equilibrium constant K for a given equilibrium reaction with substituent R and the reference K_o constant with R = H to the substituent constant σ which depends only on the specific substituent R and the reaction constant ρ which depends only on the type of reaction but not on the substituent used.

The well-known Hammett equation [20-25] takes the forms (1) and (2)

$$\log (K/K_o) = \sigma \quad \ldots (1)$$

The equation (**2**) also holds for reaction rates k of a series of reactions with substituted benzene derivatives

$$\log (k/k_o) = \sigma \rho \quad ...(2)$$

In this equation, k_o is the reference reaction rate of the unsubstituted reactant and k that of a substituted reactant. A plot of log (K/K_o) for a given equilibrium versus log (k/k_o) for a given reaction rate with many differently substituted reactants will give a straight line.

Where k and K are the rate constant and equilibrium constant respectively of the *meta*- or *para*- substituted benzene derivatives.

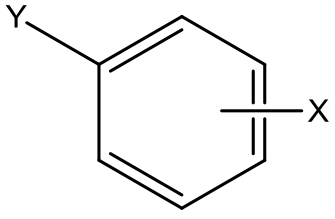


Fig-1

The k_o and K_o are the corresponding quantities of the unsubstituted compound (parent compound) of the two empirical constants in the Hammett equation, σ is substituent constant and ρ is the reaction constant.

The reaction constant, or sensitivity constant ρ, describes the susceptibility of the reaction to substituents, compared to the ionization of benzoic acid. It is equivalent to the slope of the Hammett plot. Information on the reaction and the associated mechanism can be obtained based on the value obtained for ρ.

ρ > 1, the reaction is more sensitive to substituents than benzoic acid and negative charge is built during the reaction.

0 < ρ < 1, the reaction is less sensitive to substituents than benzoic acid and negative charge is built.

ρ = 0, no sensitivity to substituents, and no charge is built.

ρ < 0, the reaction builds positive charge

Here in this research, we report a series of synthesized (*E*)-2-benzylidenehydrazine carboxamides from condensation reaction of semicarbazide with substituted benzaldehyde using acetic acid catalyst.

The synthesized hydrazone compounds have been characterized by physical constants, UV, IR and NMR spectral data. The characterized UV, IR and NMR spectral data of these (*E*)-2-benzylidenehydrazinecarboxamides have been utilized for studying the Hammett spectral correlation analyses.

2. EXPERIMENTAL

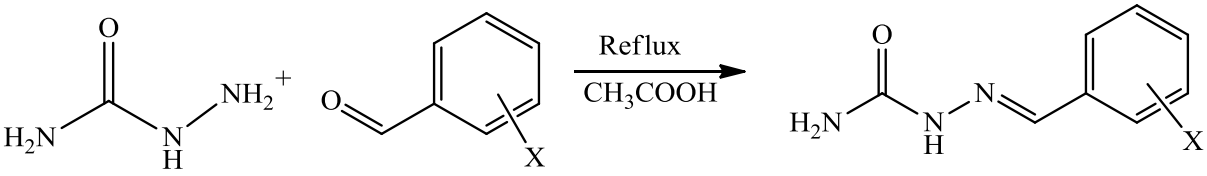
2. 1. General

The present studies for all the chemicals have been purchased from Sigma–Aldrich chemical company. All the synthesized hydrazone compounds Melting points were uncorrected by open glass capillaries on a Mettler FP51 melting point apparatus. The UV spectra of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide derivatives were recorded with ELICO-BL222 spectrophotometer (λ_{max} nm) in spectral grade methanol. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on SHIMADZU 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. 2. Synthesis of substituted hydrazone compounds

A solution of equimolar quantities of semicarbazide (0.01 mol) and substituted benzaldehydes (0.01 mol), acetic acid (two drops) and 20 mL of ethanol were refluxed for 3 hour [26]. The pale yellow solid was obtained as the final product. This crude product was recrystallized from ethanol and glittering colorless solid was obtained. The synthetic method for the substituted (*E*)-2-benzylidenehydrazinecarboxamide are given in Scheme 1. The substituted hydrazone compounds physical constants are presented in Table 1.



Where X= H, 3-Br, 4-Br, 3-Cl, 4-Cl, 4-F, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

Scheme 1. Synthesis of substituted (*E*)-2-benzylidenehydrazinecarboxamides

Table 1. Physical constants and UV, IR and NMR spectral data of substituted (*E*)-2-benzylidenehydrazinecarboxamides

Entry	X	M. F	M. W	m.p. (C)
1	H	$C_8H_9N_3O$	163.18	157-158
2	3-Br	$C_8H_8BrN_3O$	242.07	159-160 (160)[26]
3	4-Br	$C_8H_9BrN_3O$	242.07	197-198 (198)[26]
4	3-Cl	$C_8H_8ClN_3O$	197.62	179-180 (181)[26]
5	4-Cl	$C_8H_8ClN_3O$	197.62	180-181 (179)[26]
6	4-F	$C_8H_8FN_3O$	181.17	191-192
7	4-OCH_3	$C_9H_{11}N_3O2$	193.20	181-182 (180)[26]
8	4-CH_3	$C_9H_{11}N_3O$	177.20	169-170
9	3-NO_2	$C_8H_8N_4O_3$	208.17	162-163 (163)[26]
10	4-NO_2	$C_8H_8N_4O_3$	208.17	159-160 (161)[26]

3. RESULTS AND DISSCUSION

3. 1. Spectral linearity

In this present study the spectral linearity of synthesized substituted (*E*)-2-benzylidenehydrazinecarboxamides have studied by evaluating the substituent effects. The observed UV λ_{max} (nm), infrared νC=N, the proton chemical shifts (δ, ppm) of CH=N and carbon chemical shifts (δ, ppm) of C=N spectral data of all the substituted (*E*)-2-benzylidenehydrazinecarbothioamides are presented in Table 2.

Table 2. The UV, IR and NMR spectral data of (*E*)-2-benzylidenehydrazinecarbothioamides

Entry	X	(λ_{max}, nm)	νC=N (cm^{-1})	CH=N(ppm)	C=N(ppm)
1	H	284.50	1687.71	7.894	139.26
2	3-Br	286.50	1686.20	7.886	137.47
3	4-Br	286.00	1684.63	7.804	137.89
4	3-Cl	287.00	1688.43	7.976	139.42
5	4-Cl	286.00	1688.43	7.818	137.80
6	4-F	280.00	1672.28	7.821	138.01
7	4-OCH_3	288.00	1685.70	7.789	139.64
8	4-CH_3	284.00	1674.21	7.689	146.62
9	3-NO_2	285.00	1686.50	8.408	142.23
10	4-NO_2	284.50	1683.56	8.362	143.26

3. 2. UV-visible spectral correlations

The recorded UV absorption maximum λ_{max} (nm) values of all the synthesized (*E*)-2-benzylidenehydrazinecarboxamides are presented in Table 2. This spectral values was correlated [22-25] with Hammett substituent constants and Swain-Lupton's [26] parameters. In this regression analysis the structure parameter correlation Hammett equation have been employed, as shown in equation (3).

$$\lambda = \rho\,\sigma + \lambda_0 \qquad \ldots (3)$$

where λ_0 is the frequency for the parent member of this series

Table 3. The results of statistical analysis of UV absorption maximum λ_{max} (nm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds with Hammett constants σ, σ^+, σ_I & σ_R and *F* and *R* parameters

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
λ_{max} (nm)	σ	0.900	285.13	0.054	2.332	7	3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2
	σ^+	0.900	285.18	-0.194	2.330	7	3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2

	σ_I	0.904	285.30	-0.394	2.330	7	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2
	σ_R	0.901	285.31	1.205	2.317	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2
	F	0.902	286.14	-2.442	2.239	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−F, 4−OCH_3, 3−NO_2
	R	0.901	285.35	1.095	2.314	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2

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

The results of single-liner regression analysis [22,24] are shown in Table 3. From the single-liner regression analysis, it is evident that the UV absorption maximum λ_{max} (nm) values of all the (*E*)-2-benzylidenehydrazinecarboxamides except those with parent (H), 4-F and 4-CH_3 substituents have shown better with Hammett constants σ (r = 0.900) and σ^+ (r = 0.900) parameters. The Hammett constant σ_I (r = 0.902) and *F* (r = 0.901) have also shown satisfactory correlation for all the compounds except those with 4-CH_3, 3-NO_2 and 4-NO_2 substituents. The (*E*)-2-benzylidenehydrazinecarboxamides except 4-F and 4-CH_3 have shown satisfactory correlations with Hammett constant σ_R (r = 0.901) and *R* (r = 0.901) parameters. When these substituents that have been given exception are included in regression they reduce the correlations considerably. Some of the single linear parameter correlations plot for UV absorption maximum λ_{max} (nm) is shown in Fig. (2-4).

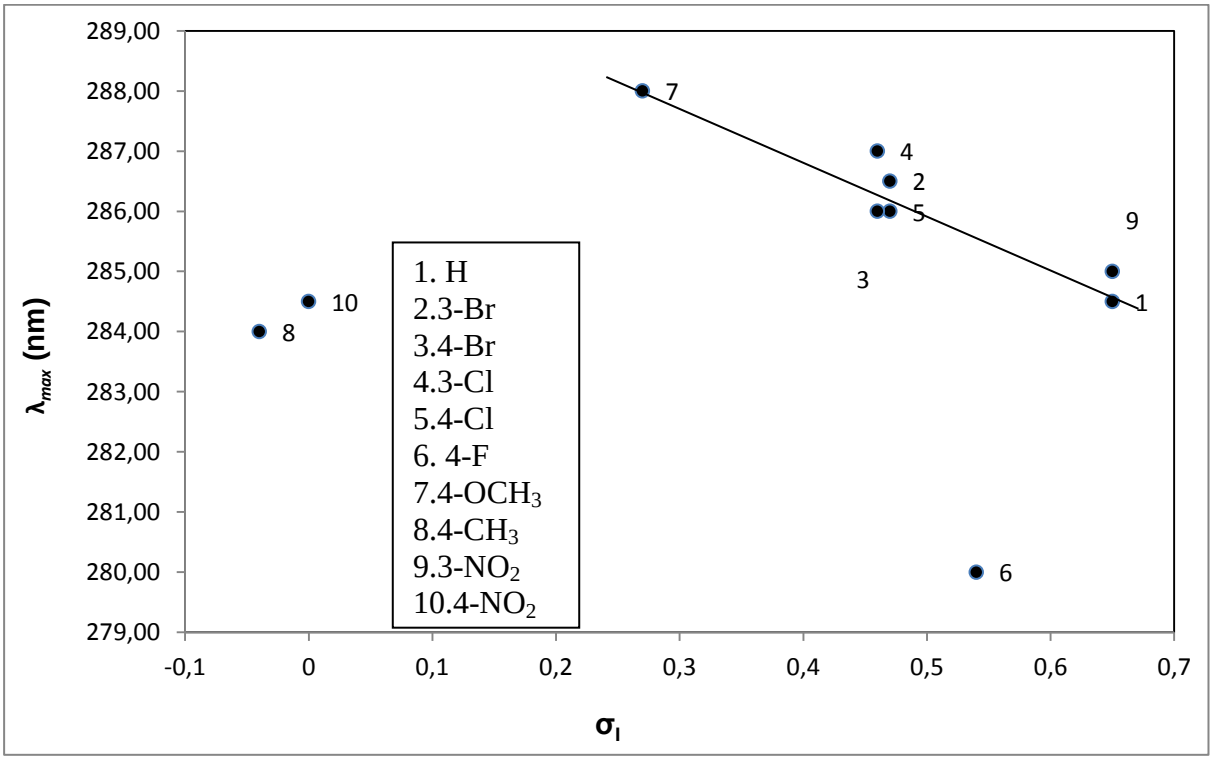


Fig. 2. Single linear plot of λ_{max}(nm) values of substituted. (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ_I

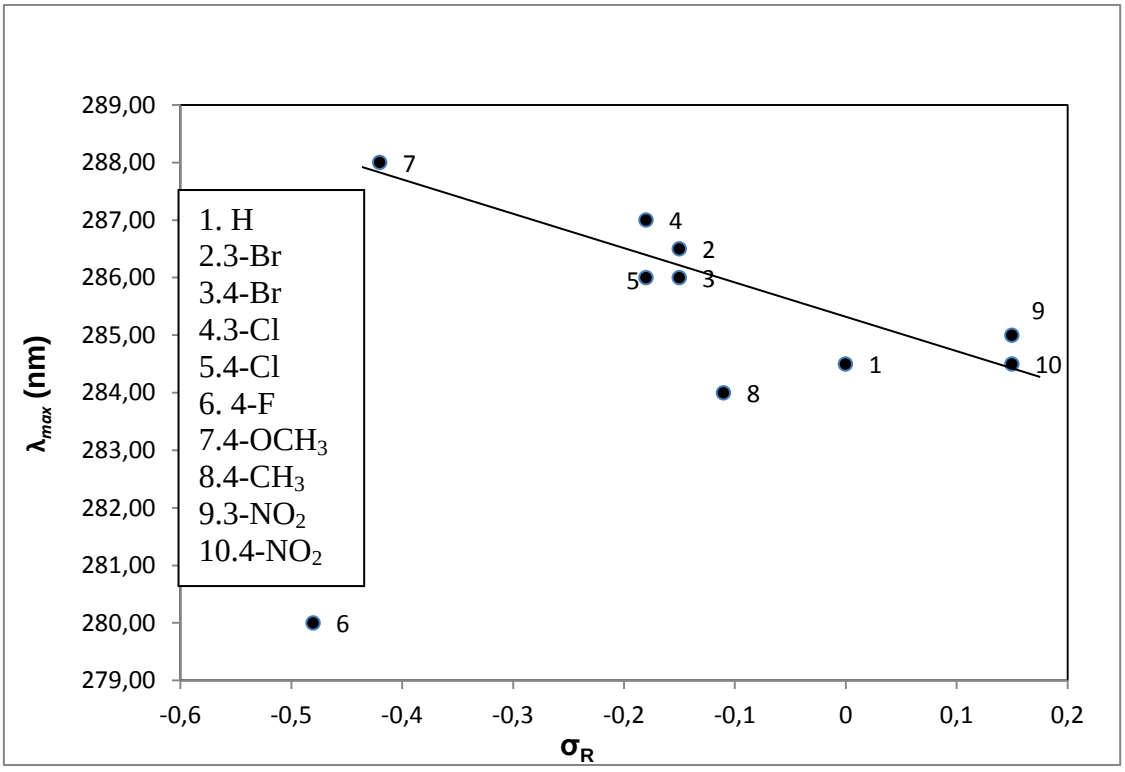


Fig. 3. Single linear plot of λ_{max}(nm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ_R

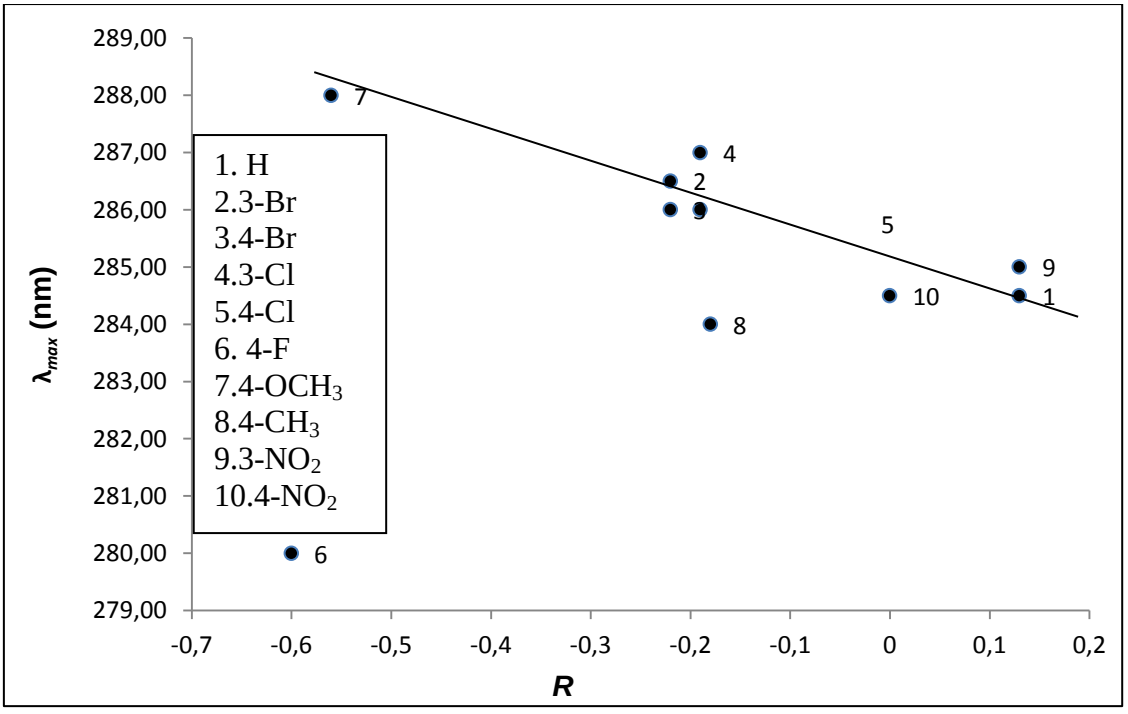


Fig. 4. Single linear plot of λ_{max}(nm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs *R*

In single linear parameter correlation with respect Hammett substituent constants and F and R parameters gave satisfactory correlations. However the multi-correlation analysis reveals satisfactory correlations as shown in equations (4) and (5).

$$UV\ \lambda_{max\ (nm)} = 285.54\ (\pm 1.706) - 0.54\ (\pm 0.034)\ \sigma_I + 1.29\ (\pm 0.401)\sigma_R \quad \ldots(4)$$
$$(R = 0.912,\ n = 10,\ P > 90\%)$$

$$UV\ \lambda_{max\ (nm)} = 286.32\ (\pm 1.591) - 2.40\ (\pm 0.315)\ F - 1.01(\pm 0.321)R \quad \ldots(5)$$
$$(R = 0.930,\ n = 10,\ P > 90\%)$$

3. 3. IR Spectral correlation

The infrared stretching frequency νC=N (cm^{-1}) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds are presented in Table 2. These infrared stretching frequency νC=N (cm^{-1}) values are correlated with different Hammett substituent constants and *F* and *R* parameters using single-linear and multi-linear regression analyses according to the approach of Jaffe [27]. The structure parameter correlation involving group frequencies, the employed Hammett equation is shown in equation (6).

$$\nu = \rho\sigma + \nu_o \quad \ldots (6)$$

where ν_o is the frequency for the parent member of this series.

Table 4. The results of statistical analysis of infrared frequencies νC=N (cm^{-1}) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds with Hammett constants σ, σ^+, σ_I & σ_R and *F* and *R* parameters

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
C=N(cm^{-1})	σ	0.833	1682.47	5.519	5.77	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F,4−OCH_3, 4−CH_3, 3−NO_2,4−NO_2
	σ^+	0.931	1683.13	3.745	5.82	7	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 3−NO_2, 4−NO_2
	σ_I	0.817	1682.14	4.119	6.033	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F,4−OCH_3, 4−CH_3,3−NO_2,4−NO_2
	σ_R	0.864	1685.16	10.249	5.697	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F,4−OCH_3, 4−CH_3,3−NO_2,4−NO_2
	F	0.807	1684.47	-1.728	6.108	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F,4−OCH_3, 4−CH_3,3−NO_2,4−NO_2

	R	0.804	1685.62	9.78	5.565	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F,4−OCH_3, 4−CH_3,3−NO_2,4−NO_2

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

The results of statistical analysis of substituent effect on the infrared stretching frequency νC=N (cm^{-1}) values of all substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds are presented in Table 4. From Table 4, it is evident that the infrared stretching frequency νC=N(cm^{-1}) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds except those with 4-F, 4-OCH_3 and 4-CH_3 substituents have shown satisfactory correlation with Hammett substituent constant σ^+ (r = 0.931) only. When these substituents that have been given exception are included in regression they reduce the correlations considerably

The remaining Hammett substituent constants σ, σ_I, σ_R and *F* and *R* parameters have shown poor correlations (r < 0.900). The poor correlation is attributed to the weak inductive, resonance and field effect of the substituents unable to predict the reactivity on the frequency through resonance as per the conjugative structure (5). All the single-linear correlation analysis gave positive ρ values.

The single linear plot of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ^+ presented in Fig. 5.

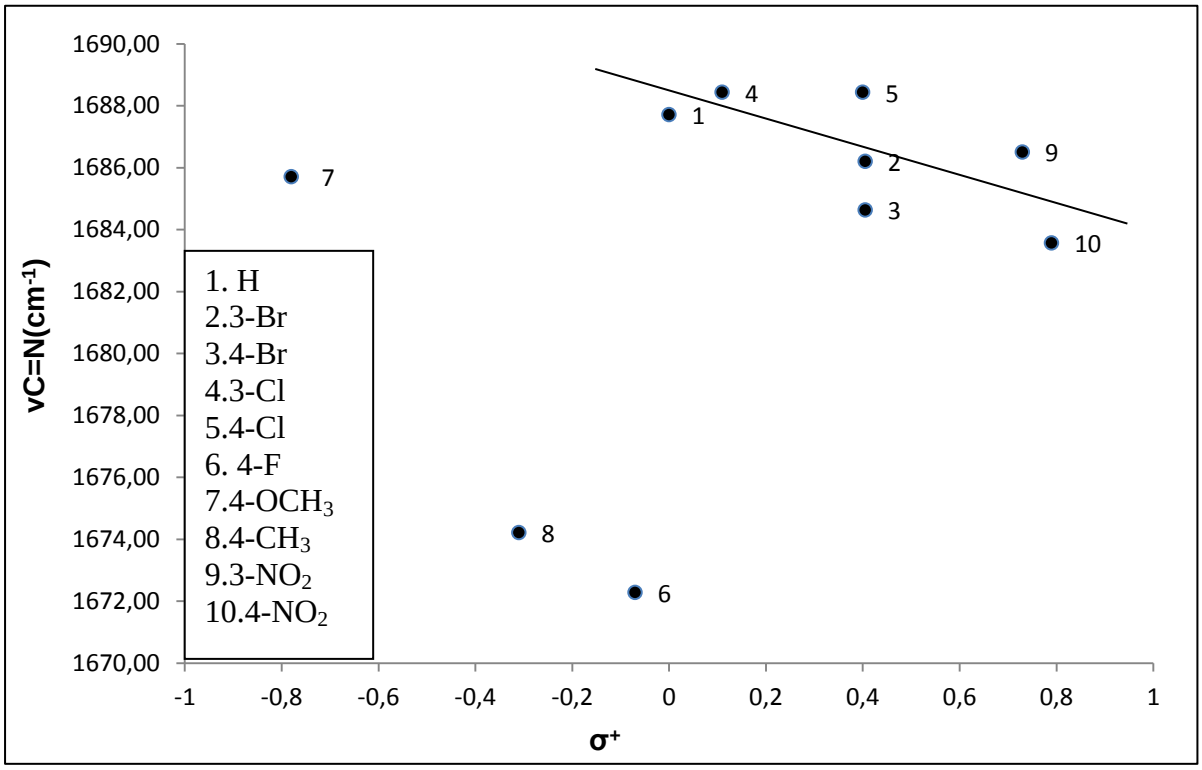


Fig. 6. Single linear plot of νC=N (cm^{-1}) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ^+

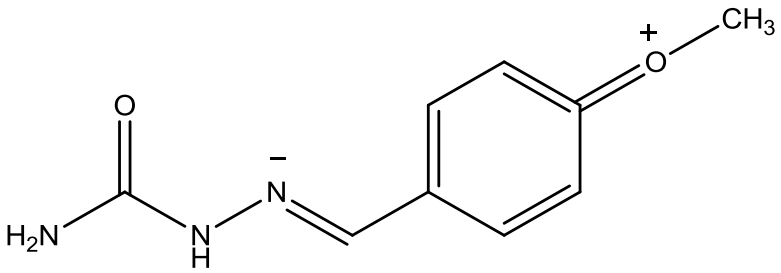


Fig. 5. The resonance - conjugative structure

This means that there is a normal substituent effect operating in all the systems. Since most of the single regression analyses, have shown poor correlations with Hammett constants and *F* and *R* parameters, it is decided to go for multi regression analyses. However the multi-regression analysis of (*E*)-2-benzylidenehydrazinecarboxamides with inductive, resonance and Swain-Lupton's [26] parameters produce satisfactory correlations as shown in equations (**7**) and (8).

$$\nu C{=}N\,(cm^{-1}) = 1683.91\ (\pm\ 4.164) + 3.04\ (\pm\ 1.345)\sigma_I + 9.79\ (\pm\ 2.794)\sigma_R \quad \ldots(7)$$
$$(R = 0.938,\ n = 10,\ P\ 90\%)$$

$$\nu C{=}N\,(cm^{-1}) = 1686.17\ (\pm\ 3.973) - 1.36\ (\pm\ 0.787)F + 9.73\ (\pm\ 1.028)R \quad \ldots(8)$$
$$(R = 0.942,\ n = 10,\ P > 90\%)$$

3. 4. NMR spectral correlation

The ^{1}H and ^{13}C NMR spectra of all the substituted (*E*)-2-benzylidenehydrazine carboxamides under investigation are recorded in deuterochloroform solution, employing tetramethylsilane (TMS) as internal standard. In nuclear magnetic resonance spectra, the proton or the ^{13}C chemical shifts (δ, ppm) depends on the electronic environment of the nuclei concerned. The assigned CH=N proton chemical shift (δ, ppm) values of synthesized (*E*)-2-benzylidenehydrazinecarboxamides are presented in Table 2. These CH=N proton chemical shift values was correlated with reactivity parameters. Thus the Hammett equation may be used in the form as

$$\delta = \rho\sigma + \delta_0 \quad \ldots (9)$$

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

3. 4. 1. ^{1}H NMR spectral correlation

The results of single-linear statistical analysis [21-24] are presented in Table-5. From this table, it is evident that the ^{1}H NMR chemical shift CH=N (δ, ppm) values of synthesized (*E*)-2-benzylidenehydrazinecarboxamides have shown satisfactory correlation with Hammett constant and *F* and *R* parameters.

Table 5. The results of statistical analysis of ^{1}H NMR chemical shift δCH=N (ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds (Series-D) with Hammett constants σ, σ^{+}, σ_I & σ_R and *F* and *R* parameters.

Chemical shifts (ppm)	Constants	r	I	ρ	s	n	Correlated derivatives
δCH= N	σ	0.908	7.802	0.068	0.12	10	H, 3−Br, 4−Br, 3−Cl, 4−Cl,4−F, 4−OCH_3, 4−CH_3, 3−NO_2, 4−NO_2
	σ^{+}	0.907	7.880	0.381	0.17	8	H, 3−Br, 3−Cl,4−Cl,4−F, 4−CH_3, 3−NO_2, 4−NO_2
	σ_I	0.906	7.696	0.632	0.20	7	3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2
	σ_R	0.907	8.062	0.86	0.17	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−CH_3, 3−NO_2, 4−NO_2
	F	0.905	7.727	0.532	0.21	7	3−Br, 4−Br,3−Cl,4−Cl,, 4−OCH_3, , 3−NO_2, 4−NO_2
	R	0.907	8.077	0.7	0.18	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−CH_3, 3−NO_2, 4−NO_2

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

From Table 5, it is evident that the ^{1}H NMR chemical shift CH=N (δ, ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds have shown satisfactory correlations with Hammett substituent constant σ (r = 0.908).

Also, all the substituents except parent (H) and those with 4-F and 4-OCH_3 substituents have shown satisfactory correlations with *F* (r = 0.905) parameter.

All the correlations produce positive ρ values. This positive ρ values indicates that the normal substituent effect operates with respect to ^{1}H NMR chemical shift CH=N (δ, ppm) values in all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds.

Some of the single parameter correlations are shown in Fig. 7-9.

Eventhough there are satisfactory single parameter correlations with respect to Hammett constants and *F* and *R* parameters. We opt to go for multi regression analysis. The multi regression analyses of the ^{1}H NMR chemical shift δCH=N (ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds with inductive, resonance and Swain-Lupton's parameters produce satisfactory correlations as shown in equations (10) and (11).

$$\delta CH=N(ppm) = 7.84\ (\pm 0.080) + 0.55\ (\pm 0.161)\ \sigma_I + 0.78\ (\pm 0.188)\ \sigma_R \quad \ldots(10)$$
$$(R = 0.990,\ n = 10,\ P > 95\%)$$

$$\delta CH=N(ppm) = 7.85\ (\pm 0.076) + 0.56\ (\pm 0.149)\ F + 0.72(\pm 0.153)R \quad \ldots(11)$$
$$(R = 0.991,\ n = 10,\ P > 95\%)$$

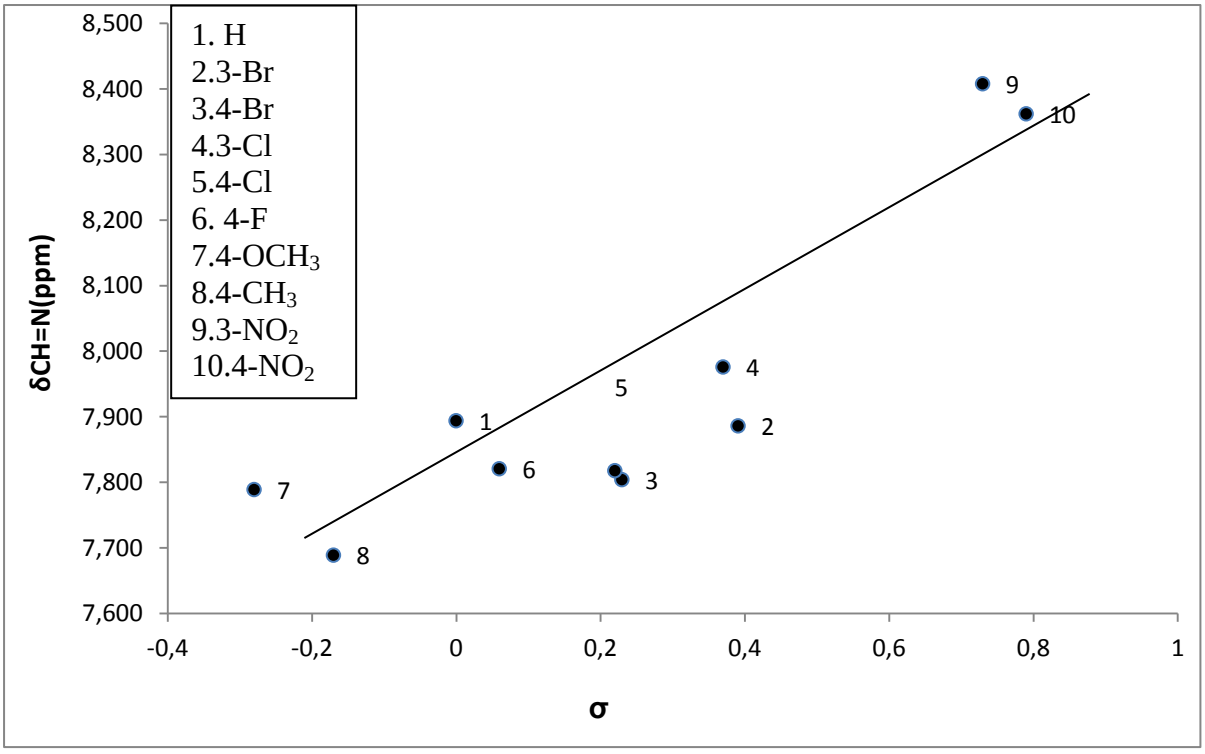


Fig. 7. Single linear plot of δCH=N(ppm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ

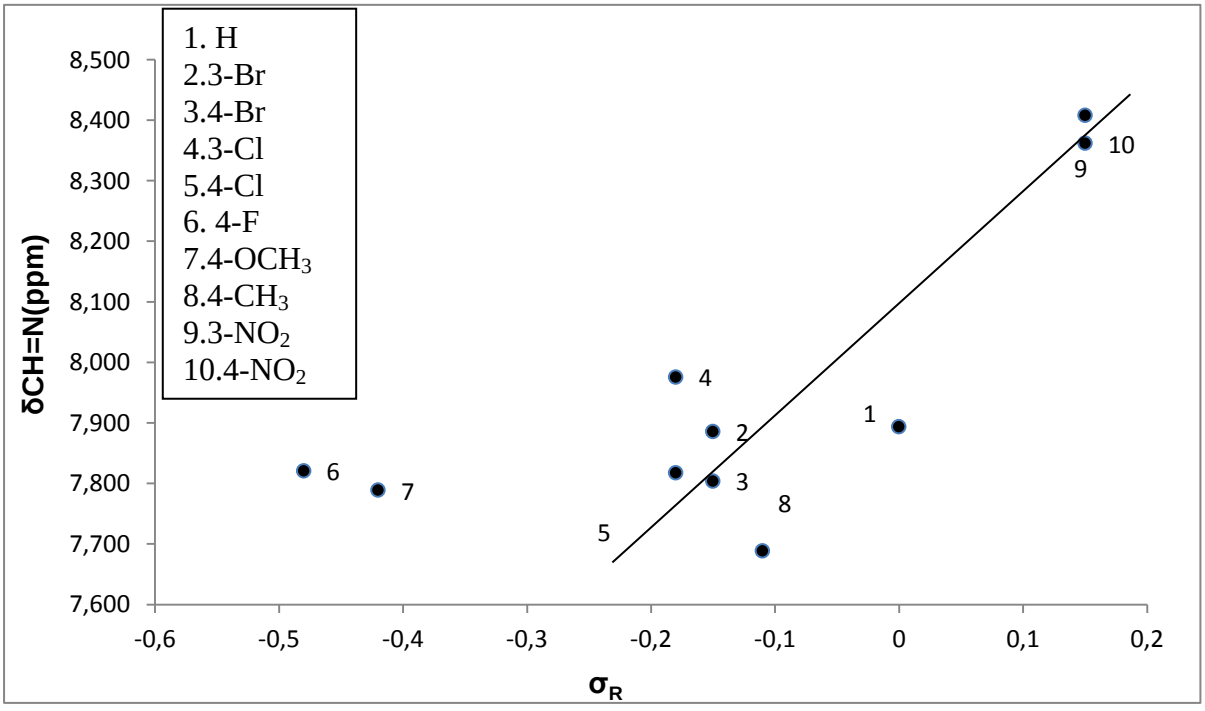


Fig. 8. Single linear plot of δCH=N(ppm) values of substituted, (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ_R

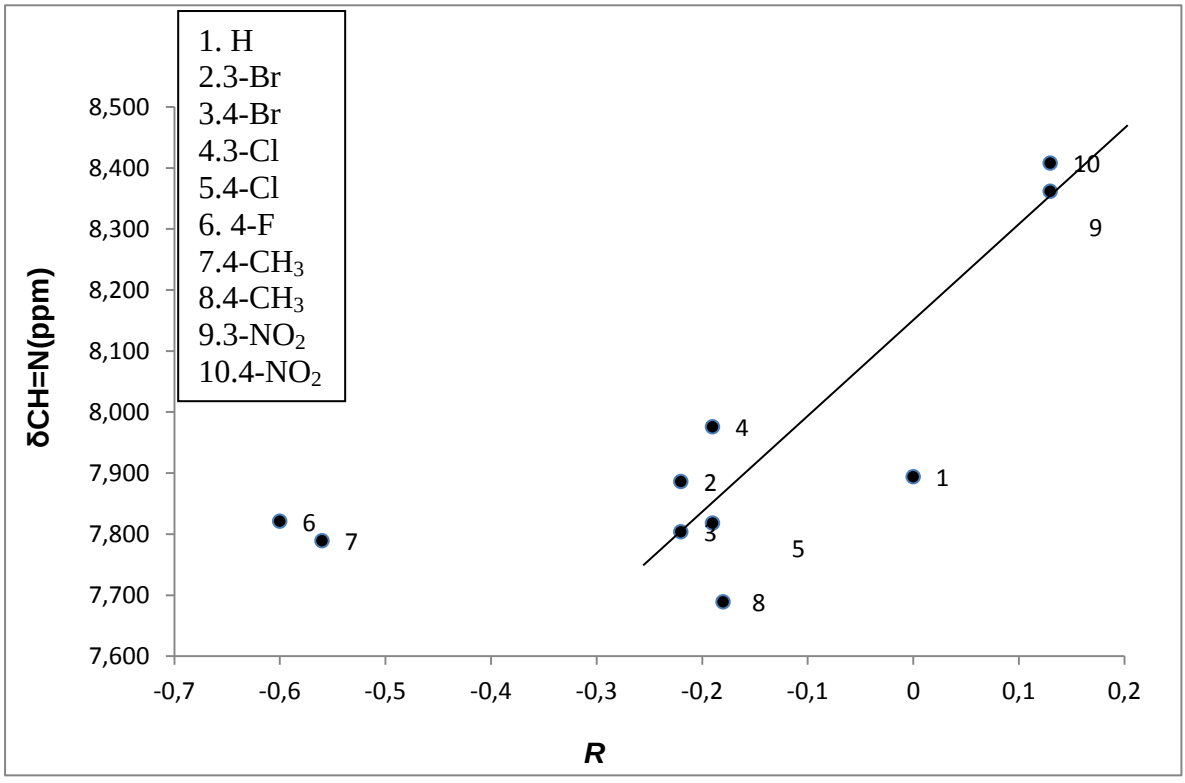


Fig. 9. Single linear plot of δCH=N(ppm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs *R*

3. 4. 2. ^{13}C NMR spectral correlation

The observed chemical shifts (δ, ppm) of C=N values have been correlated [21-24] with Hammett constants and the results of statistical analysis are presented in Table 6.

The correlation of δC=N chemical shifts (ppm) values of (*E*)-2-benzylidenehydrazinecarboxamides with Hammett substituent constants σ and σ^+ are found to be satisfactory correlation except those with 4-OCH_3 and 4-CH_3 substituents.

The ^{13}C NMR chemical shift δC=N(ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds except those with parent (H) and 4-CH_3 substituent have shown satisfactory correlations with Hammett constant σ_I(r = 0.903).

The^{13}C NMR chemical shift δC=N(ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds except that with 4-CH_3 substituent shown satisfactory correlations with Hammett constant σ_R (r = 0.904).

The ^{13}C NMR chemical shift δC=N(ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds except those with parent H, 4-F and 4- CH_3 substituents have shown satisfactory correlations with *F* (r = 0.902) parameter.

The ^{13}C NMR chemical shift δC=N(ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds except those with 4-F and 4-OCH_3 and 4-CH_3 substituents have shown satisfactory correlations with *R* (0.904) parameter.

Table 6. The results of statistical analysis of ^{13}C NMR chemical shift δC=N (ppm) values of all the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds with

Chemical shifts (δ, ppm)	Constants	r	I	ρ	s	n	Correlated derivatives
C= N	σ	0.900	140.05	0.460	3.15	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−F, 3−NO_2, 4−NO_2
	σ^+	0.900	140.16	0.024	3.15	8	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−F, 3−NO_2, 4−NO_2
	σ_I	0.903	141.60	3.681	3.01	8	3−Br, 4−Br, 3−Cl, 4−Cl, 4−F, 4−OCH_3, 3−NO_2, 4−NO_2
	σ_R	0.904	141.08	6.783	2.78	9	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 4−F, 4−OCH_3, 3−NO_2, 4−NO_2
	F	0.902	141.48	3.247	3.03	7	3−Br, 4−Br, 3−Cl, 4−Cl, 4−OCH_3, 3−NO_2, 4−NO_2
	R	0.904	141.12	5.057	2.86	7	H, 3−Br, 4−Br, 3−Cl, 4−Cl, 3−NO_2, 4−NO_2

Hammett constants σ, σ, σ_I & σ_R and *F* and *R* parameters.
r = correlation coefficient, I = intercept, ρ = slope, s = standard deviation, n = number of correlated derivatives

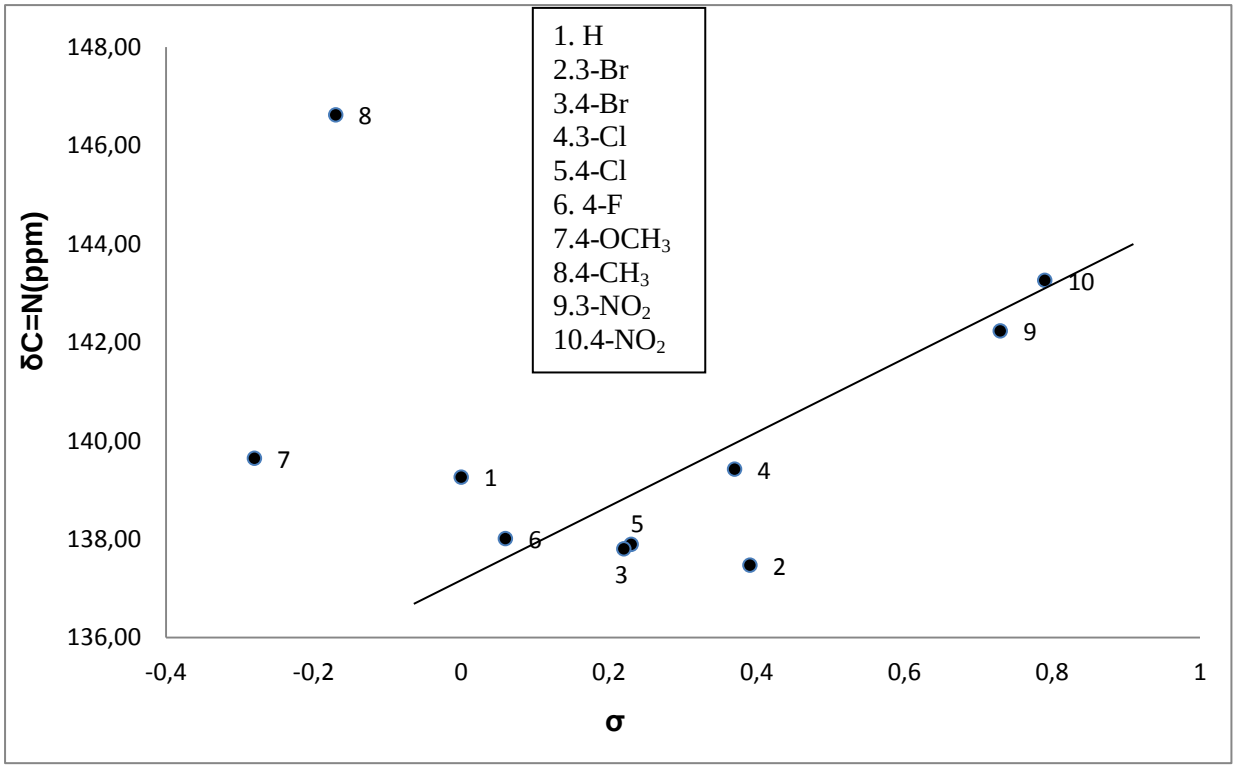


Fig. 10. Single linear plot of δC=N(ppm) values of substituted (*E*)-2- benzylidenehydrazinecarboxamide compounds Vs σ

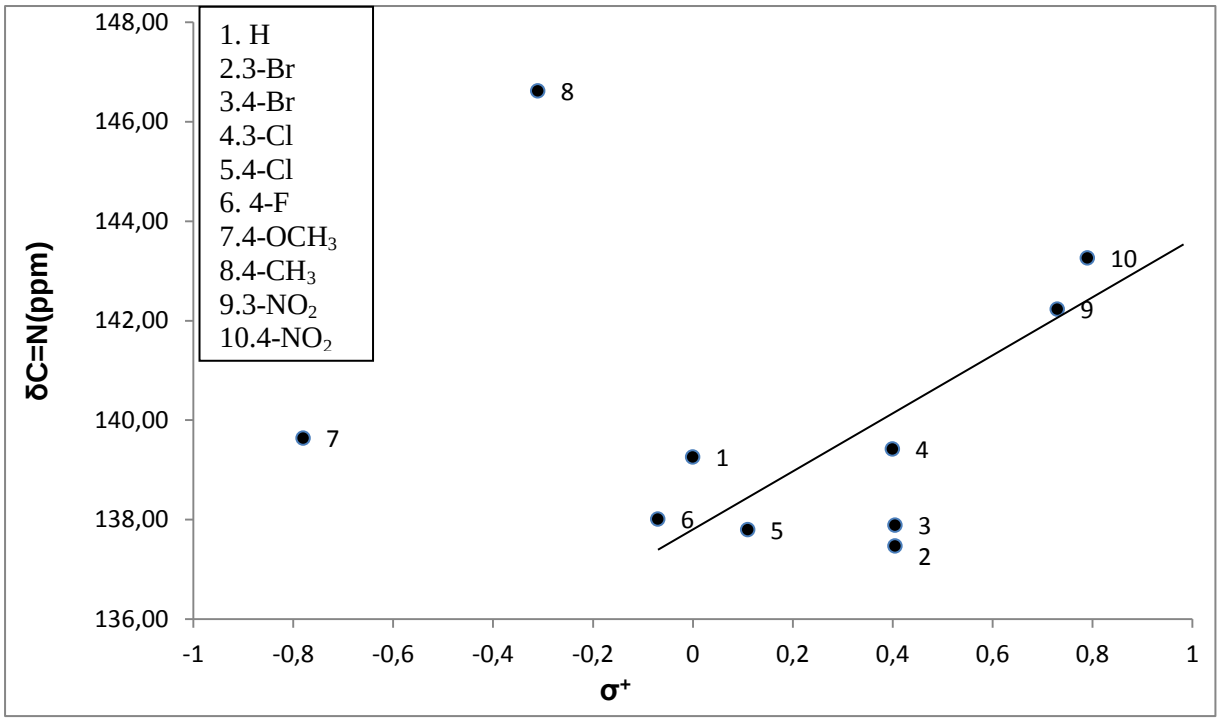


Fig. 11. Single linear plot of δC=N(ppm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs σ^+

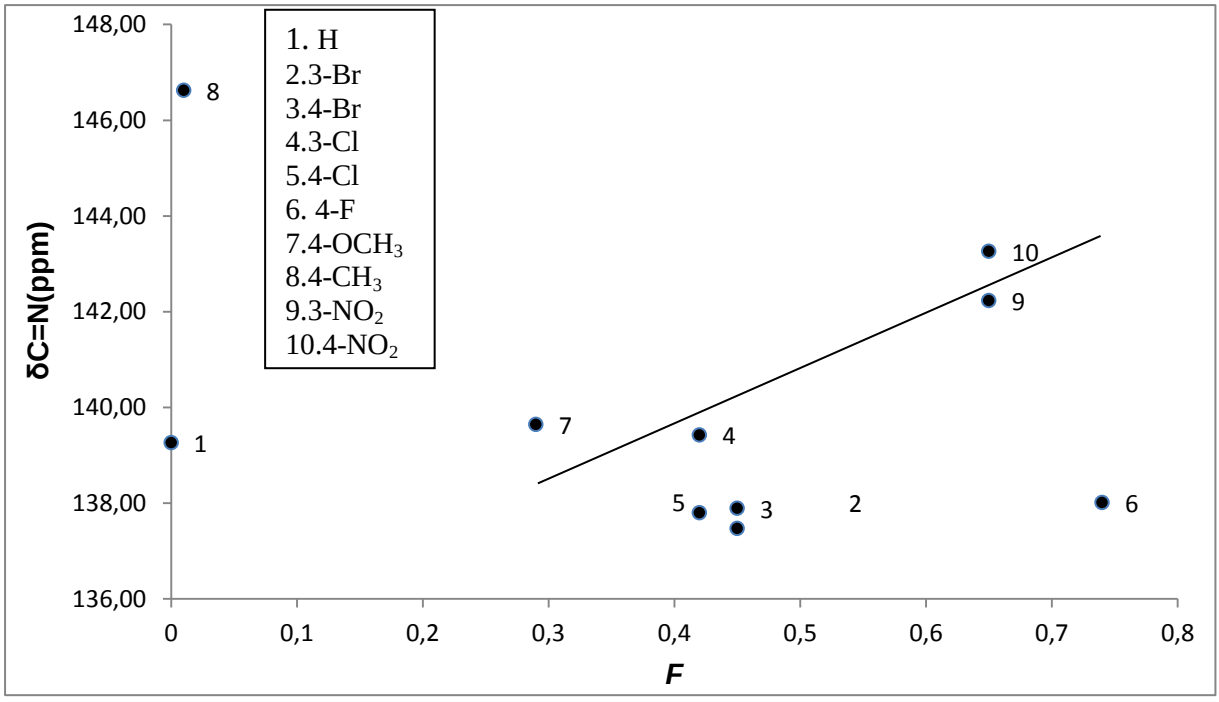


Fig. 12. Single linear plot of δC=N(ppm) values of Substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs *F*

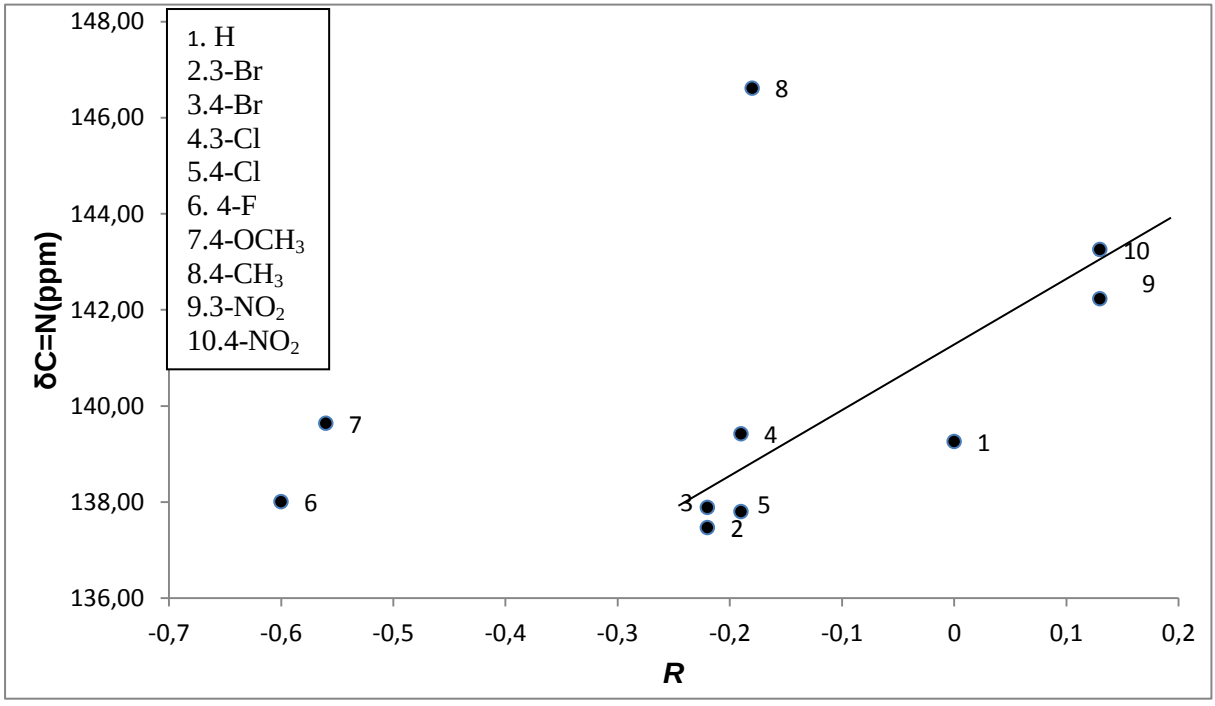


Fig. 13. Single linear plot of δC=N(ppm) values of
Substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds Vs *R*

All the substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds have shown positive ρ values. This indicates that the normal substituent effect operates with respect to ^{13}C NMR chemical shift δC=N(ppm) values of corresponding compounds. Some of the single parameter correlations are shown in Fig. 10-13.

Eventhough there are Hammett constants and *F* and *R* parameters, satisfactory single parameter correlations. We opt to go for multi regression analyses. The multi regression analyses of the ^{13}C NMR chemical shift δC=N (ppm) values of substituted (*E*)-2-benzylidenehydrazinecarboxamide compounds with inductive, resonance and Swain-Lupton's parameters produce satisfactory correlations as shown in equations (12) and (13).

$$\delta C{=}N(ppm) = 142.95\ (\pm 1.871) - 4.50\ (\pm 1.751)\ \sigma_I + 7.46\ (\pm 1.402)\ \sigma_R \quad \ldots(12)$$
$$(R = 0.956,\ n = 10,\ P > 95\%)$$

$$\delta C{=}N(ppm) = 142.35\ (\pm 1.967) - 3.05\ (\pm 1.860)F + 4.94\ (\pm 1.174)R \quad \ldots(13)$$
$$(R = 0.949,\ n = 10,\ P > 90\%)$$

4. CONCLUSIONS

The hydrazone compounds have been synthesized by condensation of semicarbazide and benzaldehydes. These hydrazone compounds have been characterized by their physical constants and spectral data. The UV, IR, NMR spectral data of these hydrazones has been correlated with Hammett substituent constants, *F* and *R* parameters.

From the results of statistical analyses the effects of substituent on the spectral data have been studied. In single linear parameter correlation the UVλ_{max}(nm) absorption produced satisfactory r values. The infrared νCH=N (cm^{-1}) frequencies except (σ^+ constant) produces poor correlation with Hammett substituent constants. The chemical shift CH=N (δ ppm) values of hydrazones gave satisfactory correlation with Hammett constants and F and R parameters. The ^{13}C NMR chemical shift C=N(δ ppm) of hydrazones is satisfactorily correlated with Hammett substituent constants namely σ, σ^+ σ_I, σ_R and *F* and *R* parameters. These constants gave satisfactory correlations.

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