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Synthesis and spectral correlation studies of some substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines

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ABSTRACT

About ten substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have been synthesized. They are characterized by their analytical, ultraviolet, infrared and NMR spectral data. From infrared spectra, the CN and N+N vibrational frequencies (cm^{-1}) of the hydrazines have been assigned. From NMR spectra, the chemical shifts (δ, ppm) of CH proton and $C(C_6H_5)_2$ carbons of the hydrazines have been assigned. These data are correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. From the results of statistical analysis, the effect of substituents on the spectral data have been discussed.

***Keywords*:** (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine; IR and NMR spectra; Hammett Correlations

1. INTRODUCTION

Azines are a class of that have been receiving increasing attention in recent years for their antibacterial, antifungal and antitumor properties [1,2]. Azines have also been

extensively used in bond formation reaction [3], polymerisation [4], in the design of liquid crystal [5] and the synthesis of heterocyclic compounds [6-8]. Few studies have been done the reaction of azine is considered to be the main factor of the most interesting reactions of azines and it is predictable that may of the reactions with dienes occur with azines as well. However, in comparison with an ordinary diene, the diene part of azine, which is in fact a hetero diene, acts differently. Due to the high electronegativity of nitrogen to carbon, the electron density around nitrogen is more than the carbon and the lone pair of nitrogen also acts as a sigma donor.

On the other hand azines have generator attention because of their ability to be used in the synthesis of a wide variety of heterocyclic compounds such as pyrazole purines and pyrimidines [9-14]. Recently the synthesis of azine pigments by peroxidase catalyzed oxidative coupling has been reported [15]. The usual method for the preparation of azines involves treatment of carbonyl compounds with hydrazine hydrate and acetic acid in ethanol [16, 17]. Recently a few methods have been reported for the synthesis of azines under various conditions [18] but not of them are simple and most require elevated temperature [19] complex catalyst [20] and microwave irradiation [21]. Therefore a need to develop a convenient and mild procedure for the preparation of azines.

Schiff's bases contain the azomethine group (-R-C=N-) and the preparations of these compounds are simple and smart. The Schiff's base compounds are prepared by condensing a carbonyl compounds like aldehydes or aryl ketones with an amine, generally in aryl refluxing with alcohol [22,23]. Several studies showed that the presence of a lone pair of electrons in a SP^2 hybridized orbital of nitrogen atom of the azomethine group of considerable chemical and biological importance [24]. Schiff's base form salt by Co-ordination of the electrons on nitrogen atom of azomethine group, because they are weak base and are readily hydrolysed by mineral acids but not by aqueous alkali solutions. Aliphatic Schiff's bases are difficult to isolate due to their tendency to polymerase. The one more nitrogen atoms present in the Schiff's base compound have a unique chemical reactivity. They are used as commercially for synthesis of dyes, synthetic fibers, and medicines etc.,

Phenylene diamine Schiff's base and it is copper chloride have been elucidated by different physiochemical methods [25]. The hydroxy substituted 3-(benzylideneamino)-2-phenylquiazoline-4(3H)-one have better anti-viral activity and cytotoxicity studies are evaluated [26]. Nivorozhkin [27] have been reported the X-ray structures of N-N-bis(5-aminopyrazol-4-yl-methylene) polymethylene diamine to eight carbons, the complexes have square planar and distorted tetrahedral structure. Nickel(II), cobalt(II), manganese(II), copper(II), iron(III) and chromium(III) complexes of Schiff's base ligand N-(salicylated)-N-(O-hydroxy acetophenone) ethylenediamine have antimicrobial activities are conformed [28,29].

In earlier study reported the synthesis of novel functionalized benzimidazole derivatives shown anti-diabetic activity. Also carbomethoxy substituted benzimidazole derivatives of bis(benzoxazole) natural products isolated from a strain of streptomycin have cytotoxicity character [30]. The C=N compound prepared by ecofriendly method in earlier studies. The others using normal grinding method and classical heating by synthesis of hydrazones [31]. Within the above view, no more information's available in literature in the past for synthesis, spectral correlation analysis of the title compounds. Only available for this like of different aryl hydrazine compounds in some literature [32,33]. Therefore, the authors have taken efforts for the synthesis of (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine to study the

quantitative structure activity relationships by spectral correlation through Hammett equation with their infra-red and NMR spectral data.

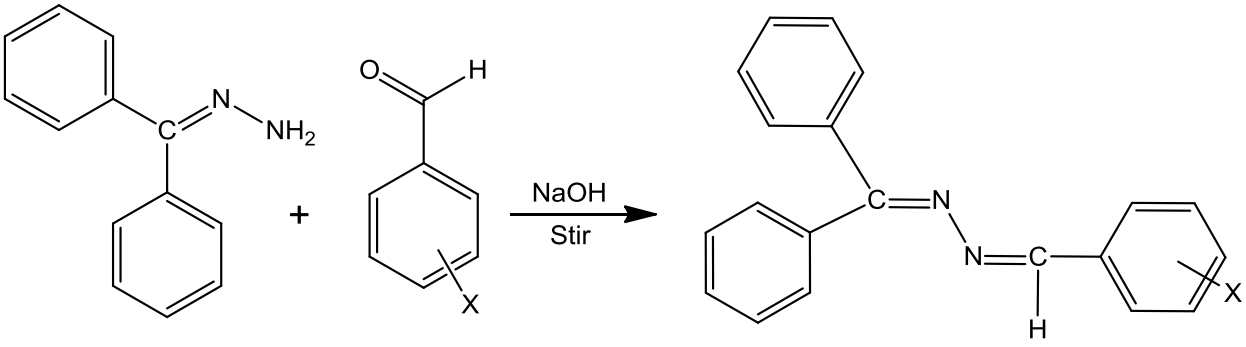
2. EXPERIMENTAL

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

2. 2. Synthesis of (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines

Appropriate mixture of 1-(Diphenylmethylene) hydrazine (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. After complete renovation of the benzaldehydes as examined by TLC, the mixture was allowed to 20 minutes for undisturbed condition. By the filtration method is used to removal of unreacted reagents. The filtrate was washed with distilled water and recrystallized from absolute ethanol, dried well, and kept in a desiccator. The purities of the compounds were examined by literature data [34].



Scheme 1. Synthesis of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines

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

Table 1. Physical constants of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines.

Entry	X	M.F.	MW	Yield (%)	M.P. (°C)	Micro analysis (%)		
						C	H	N
1	H	$C_{20}H_{16}N_2$	284	93	186-187	---	---	---
2	4-Br	$C_{20}H_{15}N_2Br$	363	91	122-123	---	---	---
3	4-Cl	$C_{20}H_{15}N_2Cl$	318	90	145-146	---	---	---
4	4-$N(CH_3)_2$	$C_{22}H_{21}N_3$	327	85	134-135	78.62 (80.70)	6.18 (6.46)	11.98 (12.83)
5	4-F	$C_{20}H_{15}N_2F$	302	89	181-182	---	---	---
6	4-OH	$C_{20}H_{16}N_2O$	300	90	97-98	69.26 (79.98)	4.99 (5.37)	9.21 (9.33)
7	4-OCH_3	$C_{21}H_{18}N_2O$	314	92	101-102	---	---	---
8	4-CH_3	$C_{21}H_{18}N_2$	298	94	120-121	---	---	---
9	3-NO_2	$C_{20}H_{15}N_3O_2$	329	98	152-153	72.14 (72.94)	4.09 (4.59)	12.28 (12.76)
10	4-NO_2	$C_{20}H_{15}N_3O_2$	320	97	158-159	---	---	---
Values in the parenthesis are calculated								

Table 2. The infrared absorptions (υ, cm^{-1}) and NMR chemical shifts (δ, ppm) spectral data of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds.

Entry	X	IR ν (cm^{-1})		^{1}H NMR (δ, ppm)	^{13}C NMR (δ, ppm)	
		C=N	N-N	C-H	C-H	C-$(Ph)_2$
1	H	1593.67	1116.27	8.301	150.66	165.74
2	4-Br	1593.88	1116.32	8.306	150.71	165.72
3	4-Cl	1593.66	1116.38	8.304	150.69	165.69
4	4-$N(CH_3)_2$	1593.17	1116.09	8.291	150.38	165.45
5	4-F	1593.88	1116.42	8.310	150.67	165.78

6	4-OH	1593.71	1116.39	8.307	150.62	165.82
7	4-OCH_3	1593.02	1116.06	8.288	150.36	165.44
8	4-CH_3	1593.12	1116.18	8.289	150.42	165.48
9	3-NO_2	1593.96	1116.88	8.326	150.98	165.88
10	4-NO_2	1593.98	1116.92	8.329	150.96	165.91

3. RESULTS AND DISCUSSION

3. 1. Spectral linearity

In the current study the spectral linearity of synthesized substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines has been studied by evaluating the substituent effects. The observed spectral data for the benzohydrazides, infrared νC=N, νN-N, the proton chemical shifts δ(ppm) of C-H and carbon chemical shifts of C-H and $C(Ph)_2$ are correlated with various substituent constants.

3. 2. IR spectral study

The assigned infrared frequencies (cm^{-1}) of νC=N, νN-N, of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazines are presented in Table 2.

The measured infrared frequency values are correlated [35-37] 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 (1).

$$\upsilon = \rho\sigma + \upsilon_o \qquad \ldots(1)$$

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

3. 2. 1. IR Spectral Correlation of νC=N (cm^{-1})

From the Table 3, it is evident that the IR frequency νC=N (cm^{-1}) values of all substituted substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have satisfactory correlations with Hammett substituent constants σ (r = 0.917), σ^+ (r = 0.947) and σ_I (r = 0.937) and *F* (r = 0.913) and *R* (r = 0.905) parameters. However, the IR frequency υC=N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds, have shown poor correlation (r < 0.900) with remaining Hammett substituent constant σ_R. This is attributed to the weak 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 positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency υC=N (cm^{-1}) values in all substituted compounds.

Table 3. The results of statistical analysis of infrared absoptions (υ, cm^{-1}) and NMR chemical shifts (δ, ppm) of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine with Hammett σ, σ^+, σ_I, σ_R and *F* and *R* parameters.

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
C=N	σ	0.917	1593.57	0.593	0.51	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.947	1593.66	0.347	0.26	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.937	1593.25	1.049	0.25	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.852	1593.74	0.694	0.33	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.913	1593.23	0.990	0.27	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.905	1593.76	0.493	0.33	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
N-N	σ	0.991	1116.36	0.562	0.14	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ^+	0.971	1116.44	0.288	0.20	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_I	0.977	1116.09	0.882	0.88	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	σ_R	0.968	1116.55	0.795	0.22	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.905	1116.09	0.804	0.21	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.906	1116.55	0.513	0.23	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

^{1}H C–H	σ	0.998	8.303	0.026	0.00	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$^+$	0.975	8.307	0.013	0.00	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$_I$	0.982	8.290	0.044	0.00	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$_R$	0.916	8.311	0.033	0.01	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	F	0.907	8.289	0.041	0.09	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	R	0.905	8.312	0.021	0.12	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
^{13}C C–H	σ	0.916	150.62	0.426	0.14	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$^+$	0.984	150.68	0.235	0.14	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$_I$	0.978	150.42	0.948	0.16	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$_R$	0.947	150.42	0.648	0.16	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	F	0.906	150.43	0.569	0.12	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	R	0.971	150.77	0.412	0.13	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
^{13}C C-(Ph)$_2$	σ	0.974	165.67	0.281	0.13	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$^+$	0.970	165.71	0.158	0.15	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$
	σ$_I$	0.969	165.53	0.470	0.13	10	H, 4-Br, 4-Cl, 4-N(CH$_3$)$_2$, 4-F, 3-OH, 4-OCH$_3$, 4-CH$_3$, 3-NO$_2$, 4-NO$_2$

	σ_R	0.905	165.76	0.362	0.15	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	F	0.966	165.52	0.439	0.13	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2
	R	0.953	165.77	0.250	0.15	10	H, 4-Br, 4-Cl, 4-N$(CH_3)_2$, 4-F, 3-OH, 4-OCH_3, 4-CH_3, 3-NO_2, 4-NO_2

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

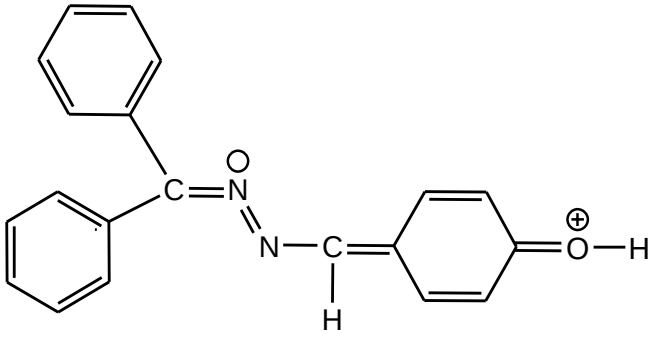


Figure 1. Resonance conjugative structure of (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine

3. 2. 2. IR Spectral Correlation of υN-N (cm^{-1})

From the Table 3, it is evident that the IR frequency υN-N (cm^{-1}) values of all substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have shown satisfactory correlations with Hammett substituent constants σ (r = 0.991), σ^+ (r = 0.971) and σ_I (r = 0.977), σ_R (r = 0.968), and *F* (r = 0.905) and *R* (r = 0.906) parameters. All the correlations have shown positive ρ values. This indicates the operation of normal substituent effect with respect to IR frequency υN-N (cm^{-1}) values in all substituted compounds. Some of the single parameter correlations failed for the IR frequency υC=N and υN-N (cm^{-1}) values with Hammett constants and *F* and *R* parameter, it is decided to go for multi regression analysis with Swain-Lupton's [38] parameters. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (2) to (5).

$$\nu C{=}N\ (cm^{-1}) = 1593.37(\pm0.171) + 0.922(\pm0.342)\sigma_I + 0.391(\pm0.344)\ \sigma_R \quad \ldots(2)$$
$$(r = 0.979,\ n = 10,\ P > 95\%)$$
$$\nu C{=}N\ (cm^{-1}) = 1593.39(\pm0.166) + 0.887(\pm0.315)F + 0.372(\pm0.221)R \quad \ldots(3)$$
$$(r = 0.0980,\ n = 10,\ P > 95\%)$$
$$\nu N{-}N\ (cm^{-1}) = 1116.27(\pm0.094) + 0.699(\pm0.187)\sigma_I + 0.566(\pm0.189)\ \sigma_R \quad \ldots(4)$$
$$(r = 0.990\ n = 10,\ P > 90\%)$$
$$\nu N{-}N\ (cm^{-1}) = 1116.27(\pm0.104) + 0.687(\pm0.198)\ F + 0.419(\pm0.139)\ R \quad \ldots(5)$$
$$(r = 0.988,\ n = 10,\ P > 95\%)$$

Some of the single plots are shown in **Figs. 2-9.**

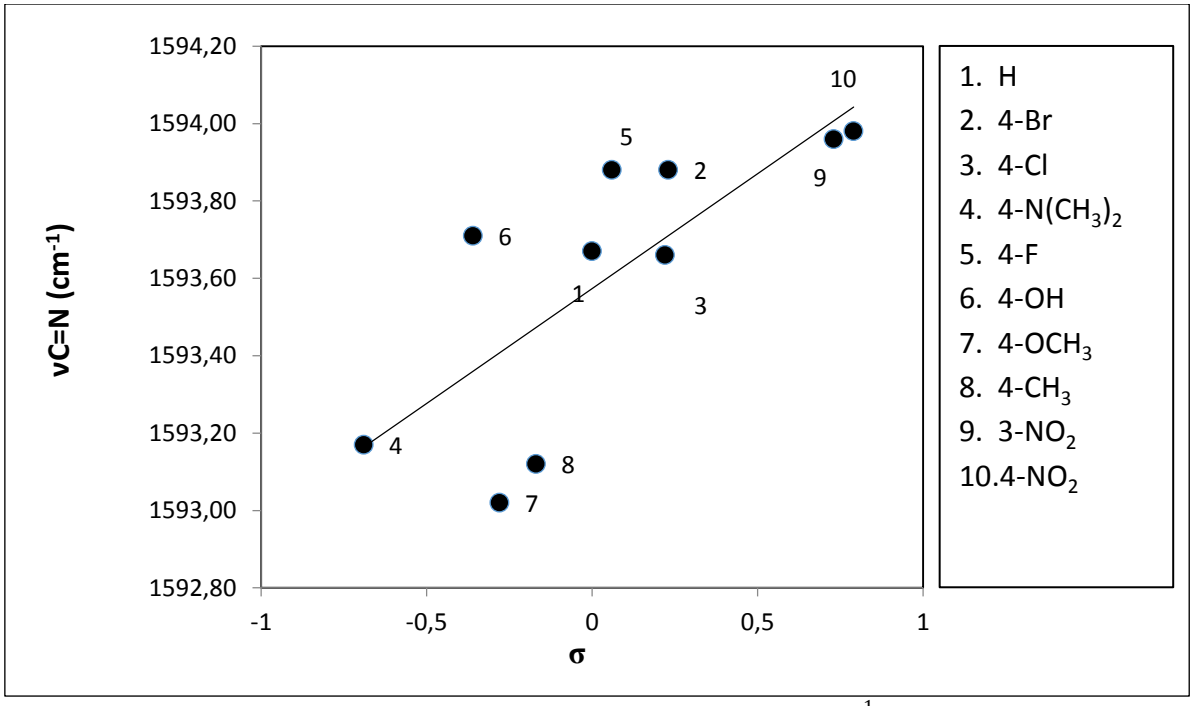


Fig. 2. Single linear plot of IR frequency νC=N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ

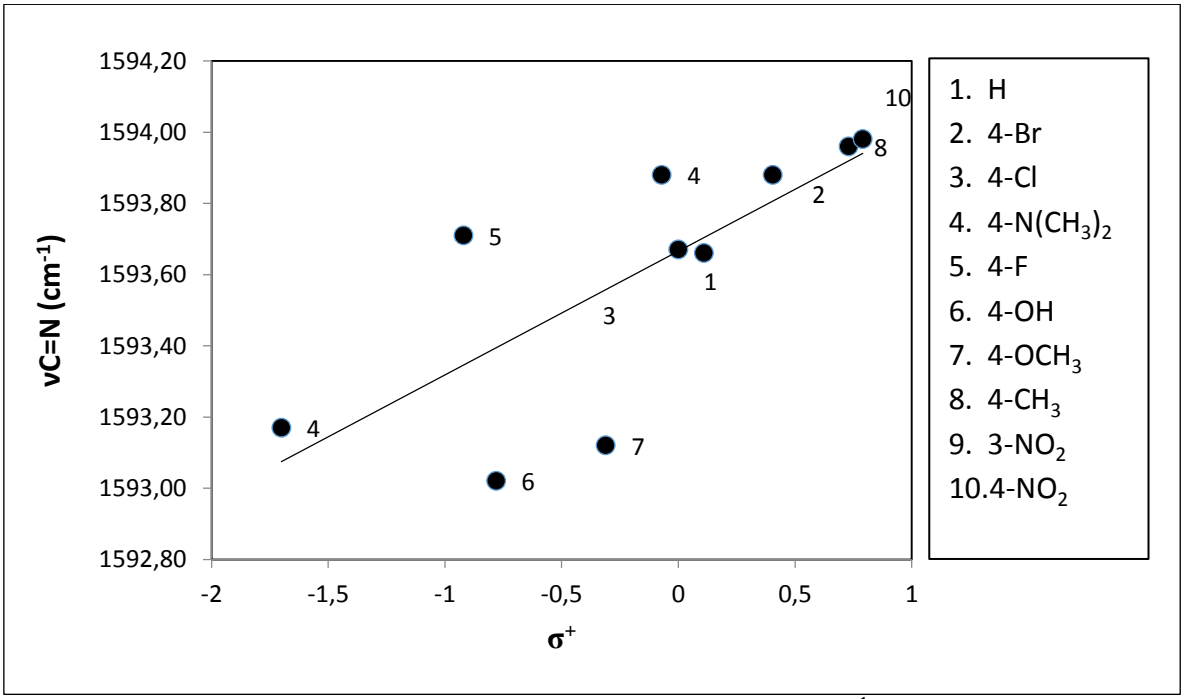


Fig. 3. Single linear plot of IR frequency νC=N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ+

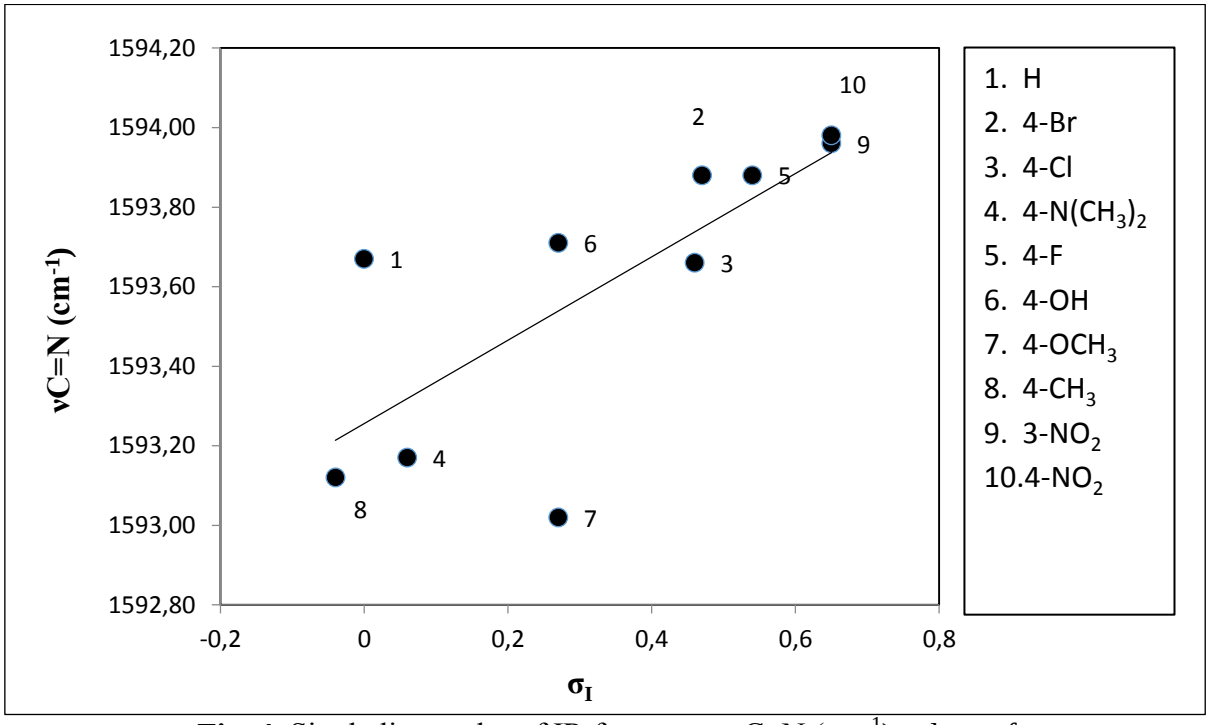


Fig. 4. Single linear plot of IR frequency νC=N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ_I

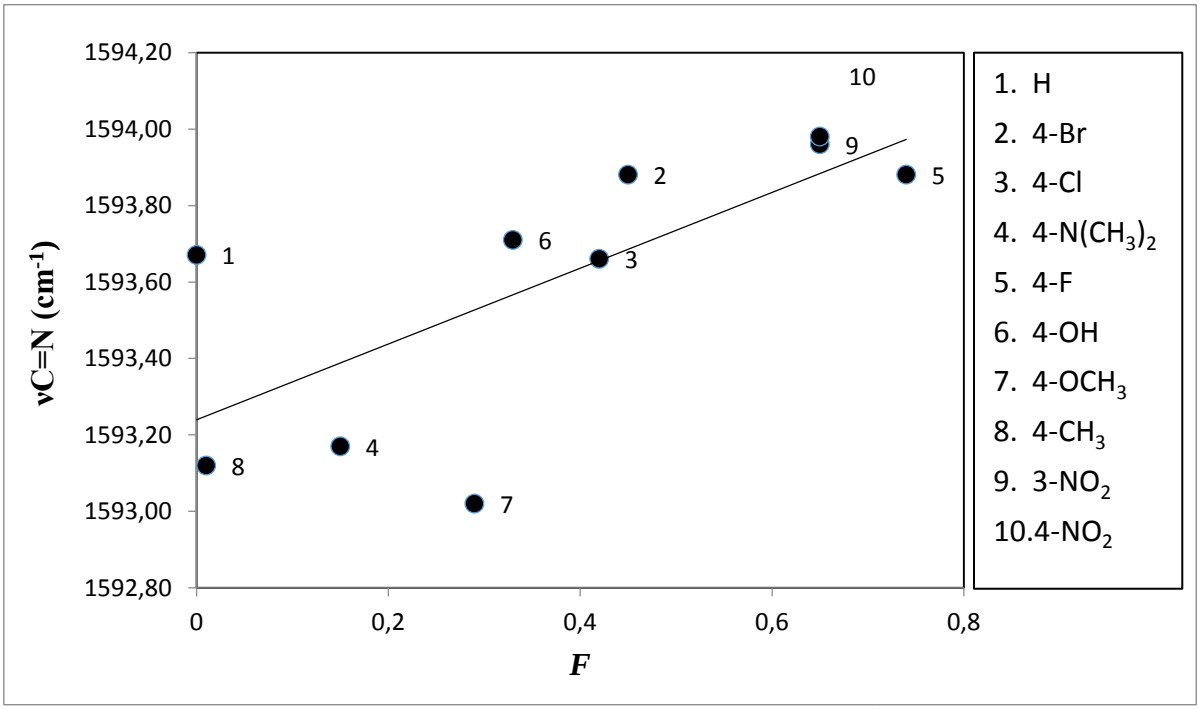


Fig. 5. Single linear plot of IR frequency νC=N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs *F*

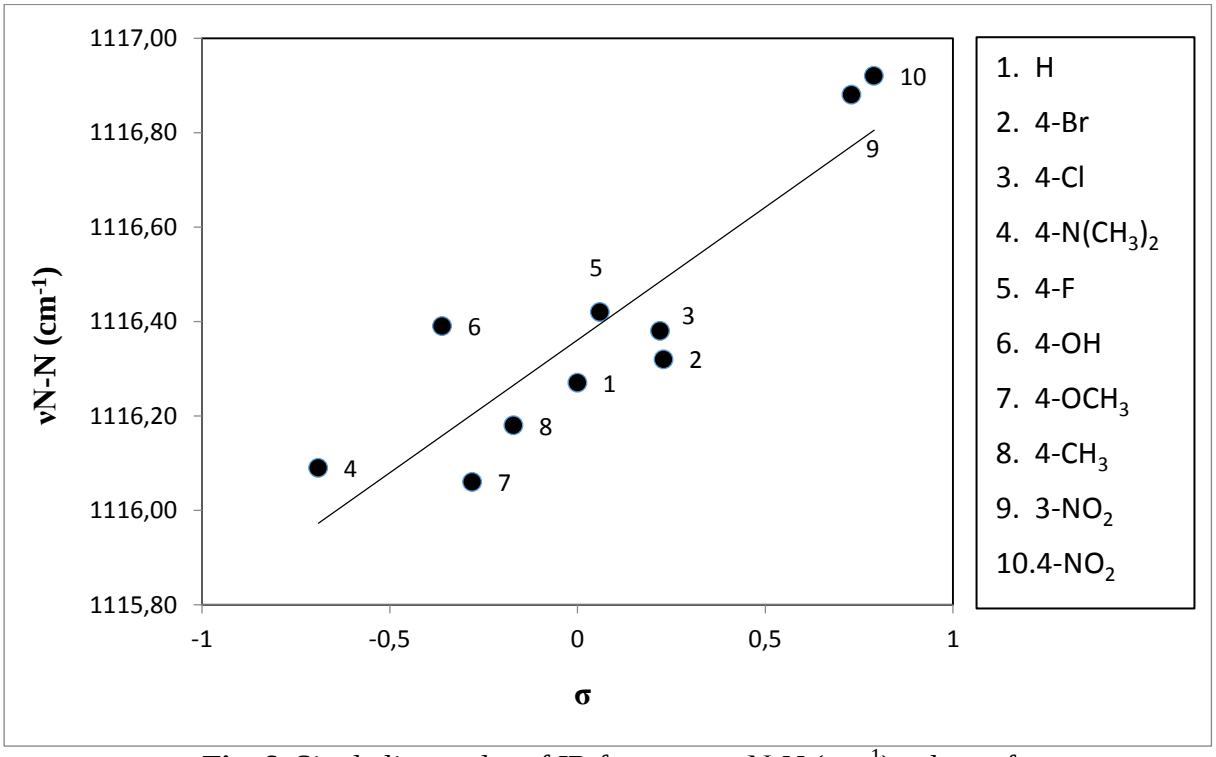


Fig. 6. Single linear plot of IR frequency νN-N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ

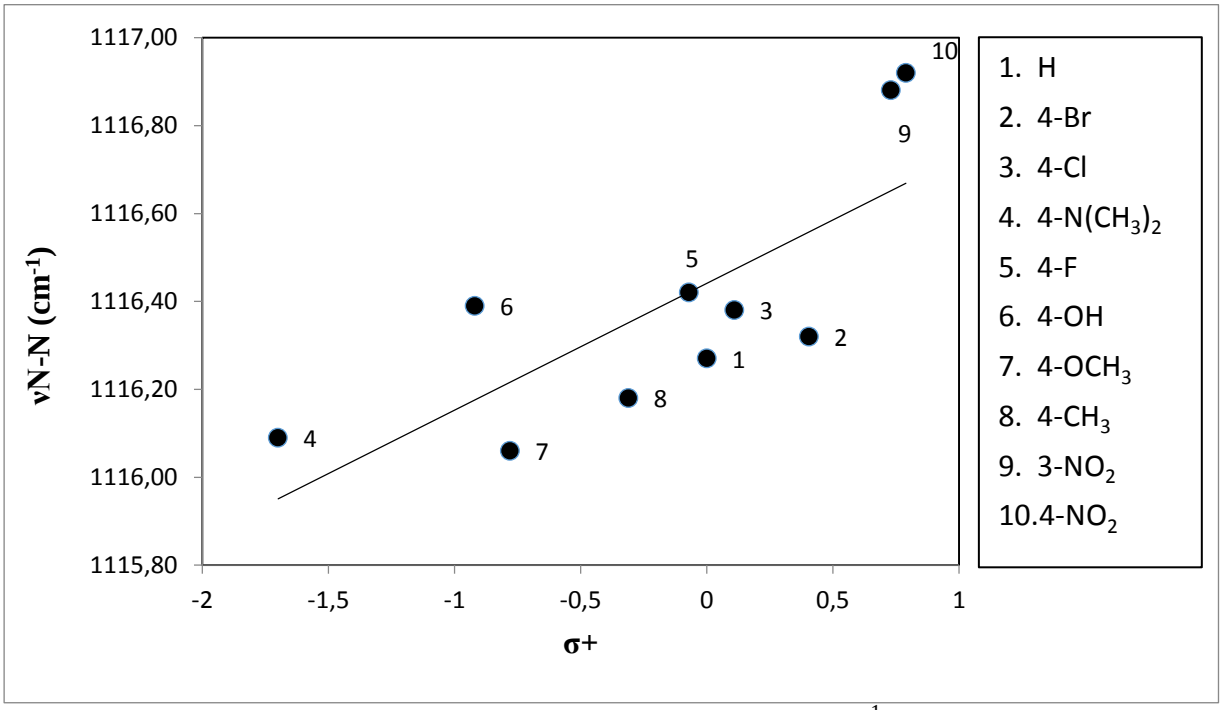


Fig. 7. Single linear plot of IR frequency νN-N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ^{+}

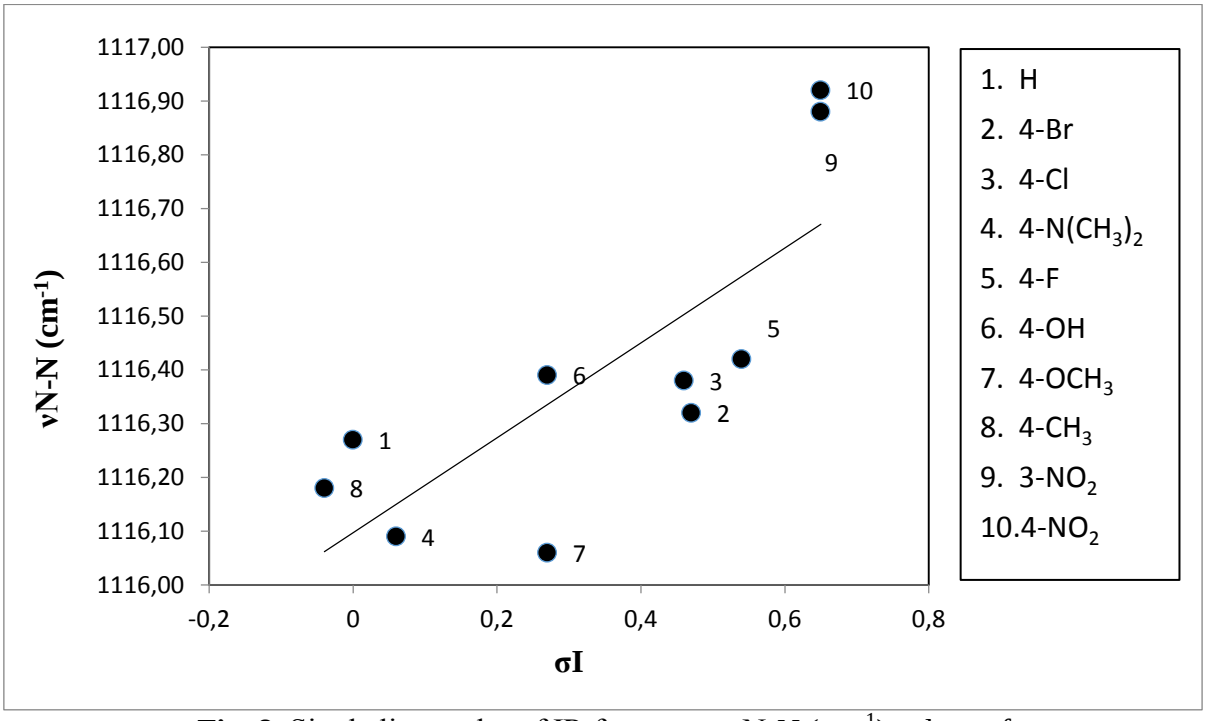


Fig. 8. Single linear plot of IR frequency νN-N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ_I

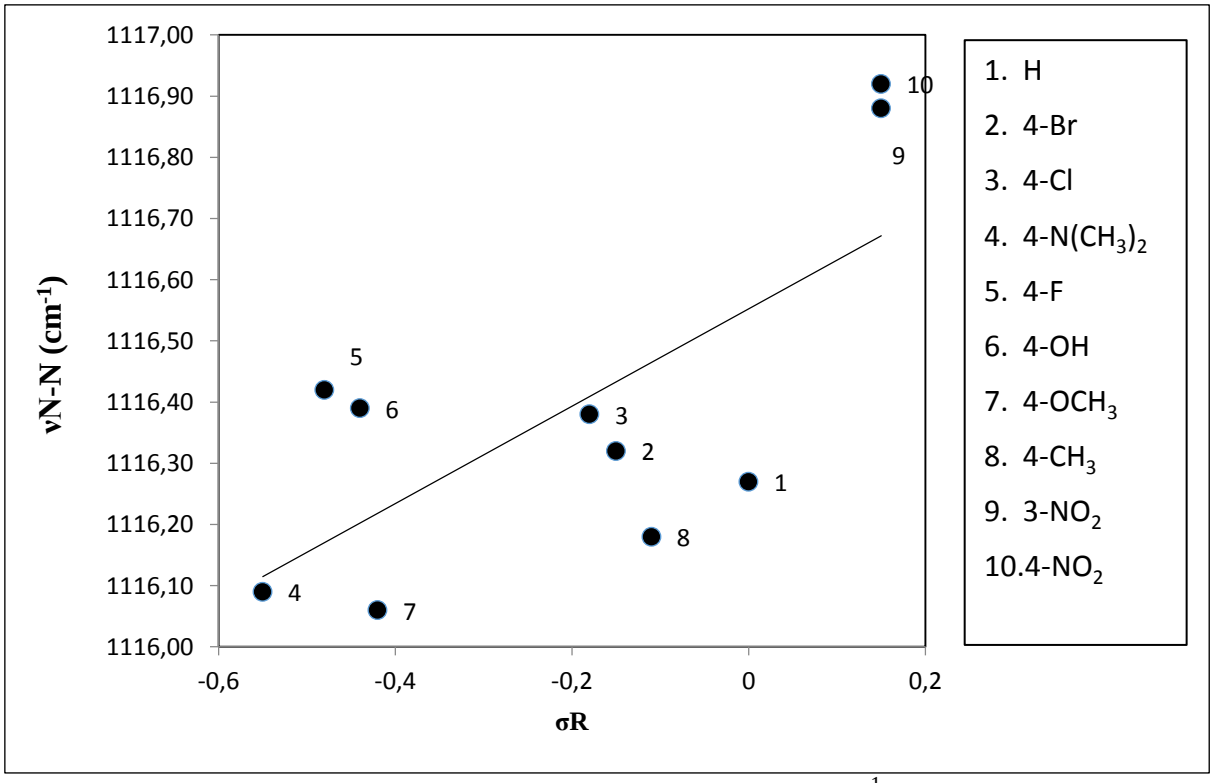


Fig. 9. Single linear plot of IR frequency νN-N (cm^{-1}) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ_R

3. 3. 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 [35-37] in the form of equation (6)

$$\delta = \rho\sigma + \delta_o \qquad \ldots(6)$$

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

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

From the Table 3, the assigned C-H chemical shifts(δ ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have shown satisfactory correlations with Hammett substituent constants σ (r = 0.998), σ^+ (r = 0.975) and σ_I (r = 0.982), σ_R (r =0.916) and *F* (r = 0.907) and *R* (r = 0.905) parameters. 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*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds.

All the single parameter correlations analyses give satisfactory correlations, for the ^{1}H – C-H chemical shifts (δ ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds with Hammett substituent constants and *F* and *R* parameter, and also go for multi regression analysis with Swain-Lupton's [38] parameters. While seeking the multi regression analysis there is satisfactory correlations are observed as shown in the following equations (7) and (8).

$$\delta\text{-H(ppm)} = 8.296(\pm0.004) + 0.037(\pm0.009)\sigma_I + 0.021(\pm0.009)\sigma_R \qquad \ldots(7)$$
$$(r = 0.990,\ n = 10,\ P > 95\%)$$
$$\delta\text{-H(ppm)} = 8.296(\pm0.004) + 0.037(\pm0.009)\ F + 0.016(\pm0.006)R \qquad \ldots(8)$$
$$(r = 0.989,\ n = 10,\ P > 95\%)$$

3. 3. 2. ^{3}C NMR Spectral Correlation

3. 3. 2. 1. ^{13}C NMR Spectral Correlations of C-H (ppm)

From the Table 3, the assigned C-H chemical shifts (δ, ppm) values of (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have shown satisfactory correlations with Hammett substituent constants σ (r = 0.916), σ^+ (r = 0.984) and σ_I (r = 0.978), σ_R (r = 0.947) and *F* (r = 0.906) and *R* (r = 0.971) parameters.

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*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds.

3. 3. 2. 2. ^{13}C NMR Spectral Correlations of C-$(Ph)_2$ (ppm)

From the Table 3, the assigned C-$(Ph)_2$ chemical shifts(δ ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds have shown satisfactory

correlations with Hammett substituent constants σ (r = 0.974), σ^+ (r =0.970) and σ_I (r = 0.969), σ_R (r = 0.905) and *F* (r = 0.966) and *R* (r = 0.953) parameters.

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*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds. Some of the single parameter correlations are illustrated in Figs. 10-13.

All the single parameter correlations analyses give satisfactory correlations, for ^{13}C C-H and C-$(Ph)_2$ chemical shifts (δ, ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds with Hammett substituent constants and *F* and *R* parameters in the following equations (9 to 12).

$$\delta C\text{-}H(ppm) = 150.567(\pm 0.060) + 0.504(\pm 0.121)\sigma_I + 0446(\pm 0.122)\sigma_R \quad \ldots(9)$$
$$(r = 0.993,\ n = 10,\ P > 90\%)$$
$$\delta C\text{-}H(ppm) = 150.580(\pm 0.0681) + 0.472(\pm 0.129)F + 0.347(\pm 0.090)R \quad \ldots(10)$$
$$(r = 0.991,\ n = 10,\ P > 95\%)$$
$$\delta C\text{-}(Ph)_2(ppm) = 165.606(\pm 0.086) + 0.394(\pm 0.171)\sigma_I + 0.233(\pm 0.172)\sigma_R \quad \ldots(11)$$
$$(r = 0.977,\ n = 10,\ P > 95\%)$$
$$\delta\ \delta C\text{-}(Ph)_2(ppm) = 165.611(\pm 0.084) + 0.385(\pm 0.160)F + 0.197(\pm 0.112)R \quad \ldots(12)$$
$$(r = 0.978,\ n = 10,\ P > 95\%)$$

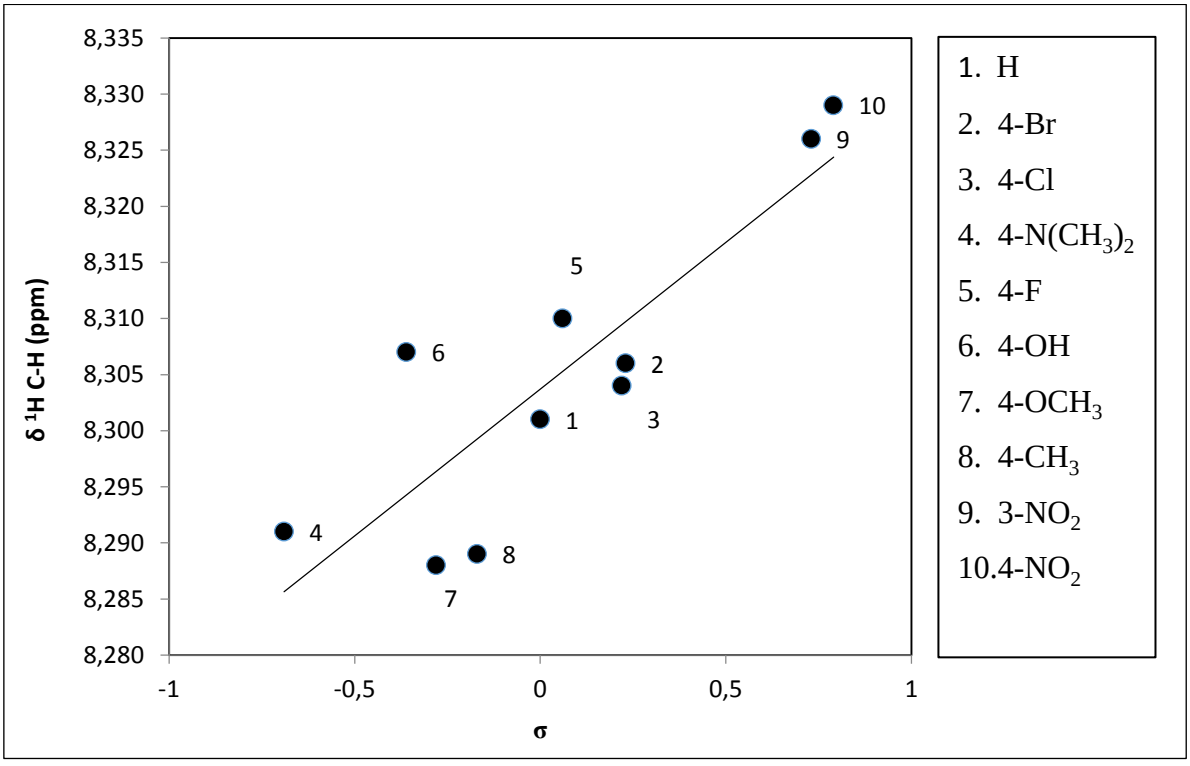


Fig. 10. Single linear plot of ^{1}H NMR δ C-H (ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ

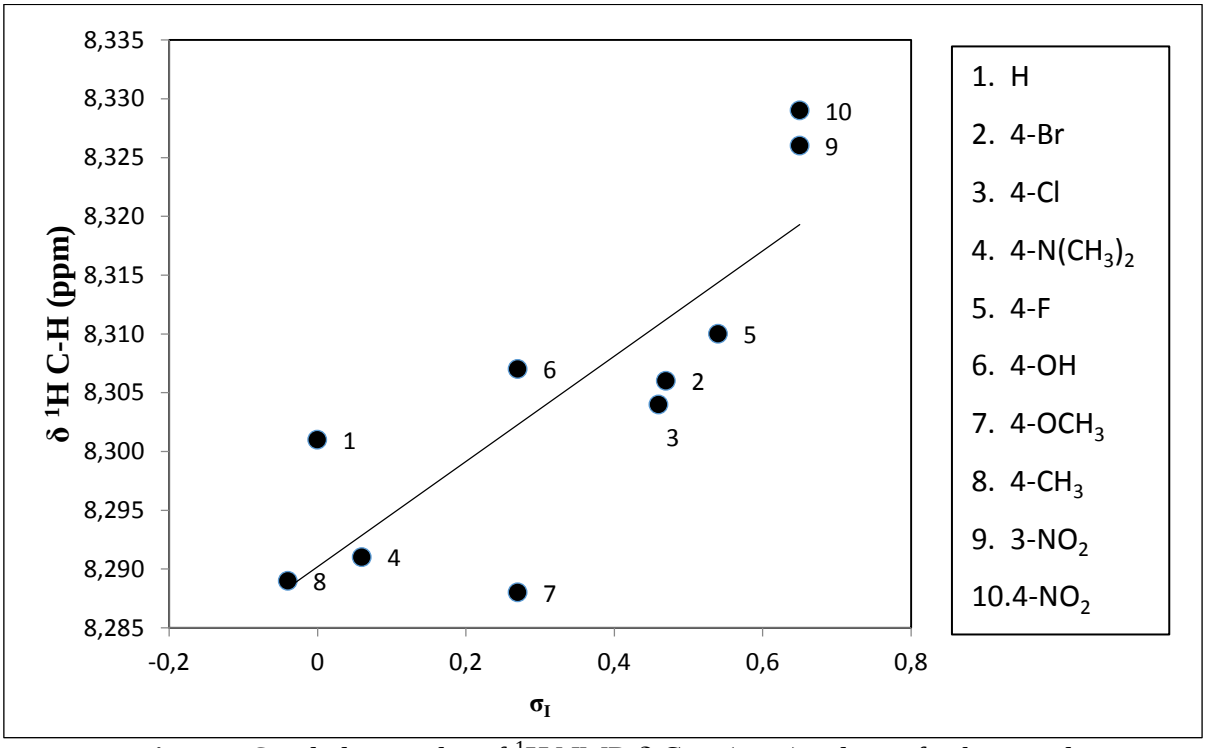


Fig. 11. Single linear plot of ^{1}H NMR δ C-H (ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ_I

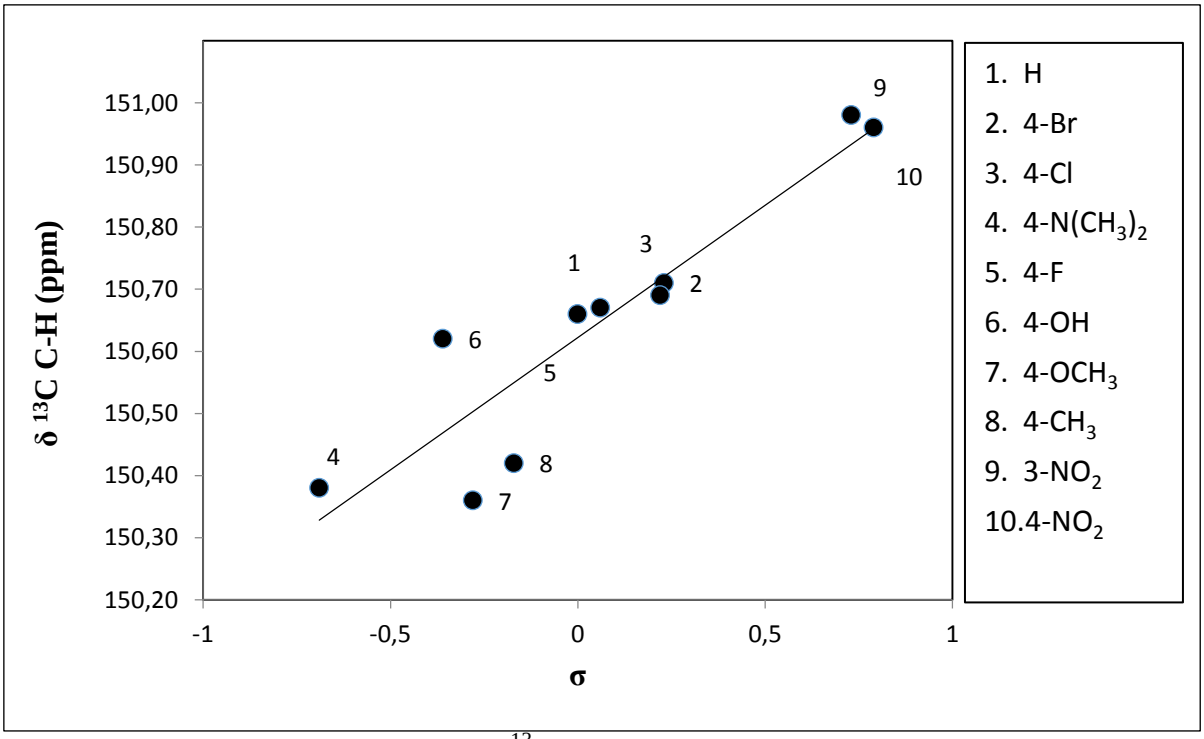


Fig. 12. Single linear plot of ^{13}C NMR δ C-H (ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ

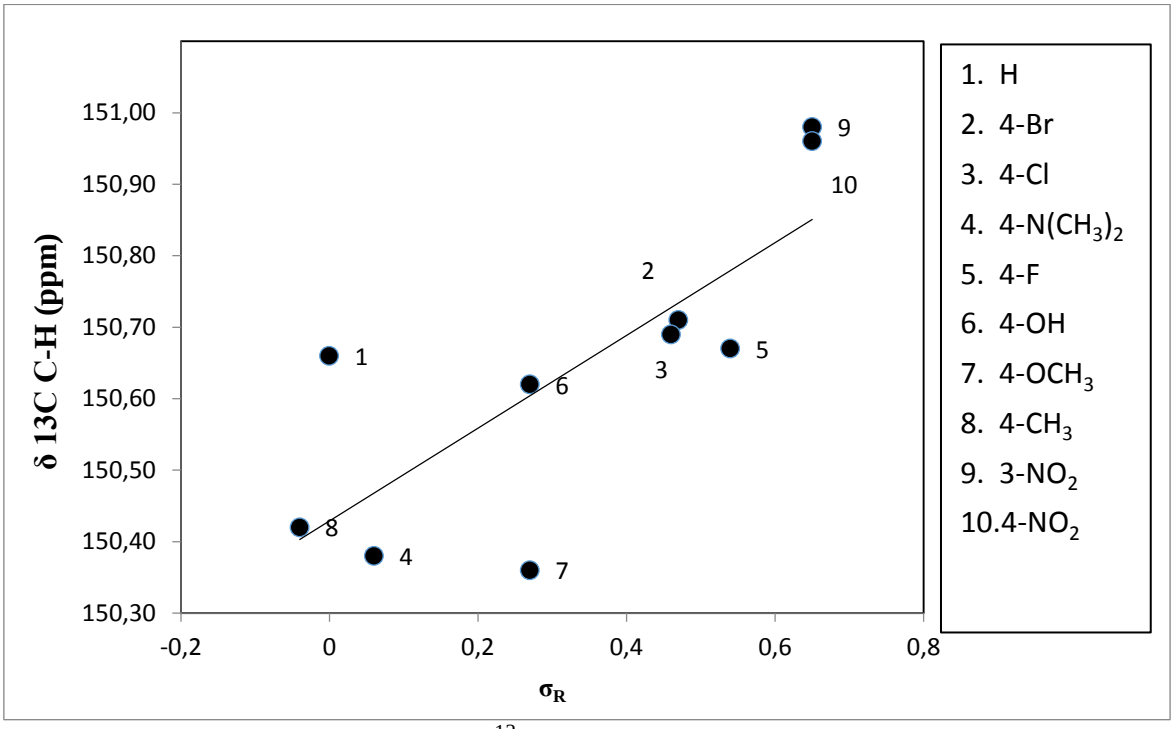


Fig. 13. Single linear plot of ^{13}C NMR δ C-H (ppm) values of substituted (*E*)-1-Benzylidene-2-(diphenylmethylene) hydrazine compounds Vs σ_R

4. CONCLUSIONS

A series containing ten numbers of substituted (*E*)-1-benzylidene-2-(diphenylmethylene) hydrazine compounds have been synthesized by condensation of aryl hydrazine and substituted benzaldehydes. These synthesized substituted (*E*)-1-benzylidene-2-(diphenylmethylene) hydrazine compounds have been characterized by their physical constants, spectral data. The UV, IR, NMR spectral data of these substituted (*E*)-1-benzylidene-2-(diphenylmethylene) hydrazine 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 most number of satisfactory correlations. However, all the multi-regression analyses have shown satisfactory correlations.

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