



Hammett spectral LFER of some antioxidant substituted benzylidene hydrazines

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ABSTRACT

About nine (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines have been synthesized by hydroxy apatite catalyzed condensation of 2,4-dinitrophenyl hydrazine and substituted benzaldehydes under microwave irradiation conditions. The obtained yields of these hydrazines are more than 85%. The purities of synthesized hydrazines are examined by the analytical and spectroscopic data reported earlier. The infrared spectral C=N, NH frequencies (ν , cm^{-1}) and the NMR spectral chemical shifts of CH, NH protons and carbons are assigned and are correlated with Hammett substituent constants, F and R parameter using single and multi-regression analysis. From the results of statistical analysis the effects of substituent on the group frequencies have been discussed. The antioxidant activities of these synthesized hydrazines were measured using DPPH radical scavenging method. The hydroxy- and methoxy- substituted hydrazines shows significant antioxidant activity.

Keywords: (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines, hydroxy apatite, IR spectra, NMR spectra, Hammett correlations, antioxidant activity

1. INTRODUCTION

Hydrazones and their derivatives constitute versatile organic compounds containing azomethine functional group ($>N=N=C<$) which are distinguished from other members of this class (e.g. imines, oximes) by presence of two adjacent (N-N) atoms [1]. This two (N-N) nitrogen atoms with nucleophilic character and a carbon atom which may act as either electrophile or nucleophile according to the reaction environment [2]. They are synthesized by condensation of primary amine with carbonyl compounds (aldehydes & ketones) [3]. Many green catalysts have been used for the synthesis of hydrazone compounds like $ZnCl_2$ [4], $TiCl_2$ [5], $BiCl_3$ -K10 [6], $MgSO_4$ -PPTL [7], molecular sieves in ionic liquids [8], SiO_2 - $NaHSO_4$ [9] and PSSA [10]. Hydrazones are important intermediates in the synthesis of nitrogen-containing compounds that have been widely utilized as key synthetic intermediates in the construction of indoles [11], carbazoles [12], pyrazoles [13], indazoles [14] and thiazolidin-4-one [15]. The aryl hydrazone compounds are also used as intermediates in Mannich type reaction, asymmetric syncyanation and allylation reactions [16]. The metal complexes of hydrazones have potential applications as active materials in nonlinear optics [17], catalysts [18], magnetic materials with diverse magnetic interaction [19] and luminescent probes [20]. Many researchers had synthesized such type of compounds [21] as target molecules and evaluated their biological activities. Hydrazones was reported to possess antimicrobial [22], antitubercular [23-25], anticonvulsant [26], analgesic [27], anti-inflammatory [28], antiplatelet [29], anticancer [30,31], antifungal [32], antiviral [33], antitumoral [34], antibacterial [35] and antimalarial [36] activities. The above remarkable considerations, pharmaceutical and industrial applications encouraged us to synthesize hydrazone derivatives of 2,4-dinitrophenyl hydrazine using acetic acid as a catalyst. The synthesized 2,4-dinitrophenylhydrazone compounds have been utilized for the study of effect of substituents on IR and NMR spectroscopic data with Hammett constant using structure parameter correlation analysis and evaluated the antioxidant activities.

2. EXPERIMENTAL

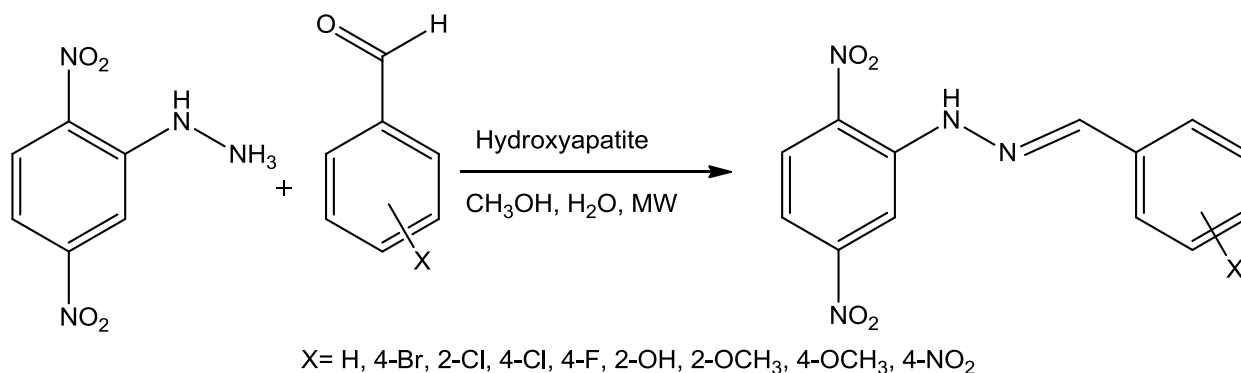
2. 1. General

The chemicals used in this present investigation were purchased from Sigma-Aldrich and Himedia chemical companies. The melting points of all synthesized compounds were found in Guna make melting point apparatus using capillary tubes. Infrared spectra (KBr , $4000-400\text{ cm}^{-1}$) were recorded on a SHIMADZU-2010 Fourier transform spectrophotometer. The NMR spectra of all hydrazines were recorded on a Bruker AV400 spectrometer operating at 400 MHz to record 1H and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent with TMS as internal standard.

2. 2. General procedure for synthesis of (E)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines

An equimolar quantity of 2,4-dinitrophenylhydrazine (2 mmol), substituted benzaldehydes (2 mmol), hydroxy apatite (0.2 g) and 4 mL of methanol have been taken in 50 mL borosil beaker and closed with lid. The mixture was stirred at room temperature for 5 min. Methanol was evaporated to give a homogeneous solid. About 5 mL of water was added to

this solid and the mixture was irradiated by microwave for the appropriate time (6-12 min) in a microwave oven at 650W (Samsung GW73BD Grill Model microwave Oven, 100-750 W, 230 V, 50 Hz, 2450 MHz) (Scheme 1) and then cooled to room temperature. After separating the organic layer with dichloromethane the solid product has been obtained on evaporation. The solid, on recrystallization with benzene-hexane mixture afforded glittering product.



Scheme 1. Synthesis of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines.

The purities of these hydrazine derivatives have been examined with their physical constants, spectral data earlier reported in literature. These data are agreeable with reported data. The analytical, physical constants and mass spectral data of these synthesized hydrazines are presented in **Table 1**.

Table 1. Physical constants, analytical and mass spectral data of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines.

No	X	M.F.	M.W.	m.p. (°C)	Mass (m/z)
1	H	C ₁₃ H ₁₀ N ₄ O ₄	286	208-209(207-208)[37]	286[M ⁺]
2	4-Br	C ₁₃ H ₉ BrN ₄ O ₄	365	264-265(263-264)[37]	365[M ⁺], 367[M ²⁺]
3	2-Cl	C ₁₃ H ₉ ClN ₄ O ₄	321	218-219(216-217)[37]	321[M ⁺], 323[M ²⁺]
4	4-Cl	C ₁₃ H ₉ ClN ₄ O ₄	321	274-275(272-273)[37]	321[M ⁺], 323[M ²⁺]
5	4-F	C ₁₃ H ₉ FN ₄ O ₄	304	279-280(280-281)[37]	304[M ⁺], 306[M ²⁺]
6	2-OH	C ₁₃ H ₁₀ N ₄ O ₅	300	260-261(261-262)[37]	300[M ⁺],
7	2-OCH ₃	C ₁₄ H ₁₂ N ₄ O ₅	316	195-196(196-197)[37]	316[M ⁺],
8	4-OCH ₃	C ₁₄ H ₁₂ N ₄ O ₅	316	254-255(253-251)[37]	316[M ⁺],
9	4-NO ₂	C ₁₃ H ₉ N ₅ O ₆	331	350-352(349-350)[37]	331[M ⁺],

The assigned infrared spectral C=N, NH frequencies (ν , cm^{-1}) and the NMR spectral chemical shifts of CH, NH protons and carbons of (*E*)-(2, 5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are presented in **Table 2**.

Table 2. Infrared and NMR spectral data of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines.

Entry	X	IR (ν , cm^{-1})		^1H NMR (δ , ppm)		^{13}C NMR (δ , ppm)	
		CN	NH	CH	NH	CH	Cipso
1	H	1619.46	3281.26	8.761	11.681	149.48	137.28
2	4-Br	1621.82	3274.17	8.627	11.682	147.49	126.48
3	2-Cl	1618.92	3284.18	8.710	11.613	148.21	135.84
4	4-Cl	1617.83	3285.01	8.692	11.623	148.81	137.63
5	4-F	1615.08	3289.18	8.710	11.658	148.86	164.32
6	2-OH	1621.80	3272.91	8.801	11.712	148.07	158.08
7	2-OCH ₃	1615.34	3271.36	8.673	11.602	145.36	156.92
8	4-OCH ₃	1615.12	3272.08	8.681	11.316	145.81	156.89
9	4-NO ₂	1623.71	3289.71	8.853	11.693	150.72	158.38

3. RESULTS AND DISCUSSION

3. 1. Infrared spectral correlations

The assigned CN and NH stretching frequencies (cm^{-1}) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines have been correlated with Hammett substituent constants and Swain-Lupton constants [38-40]. In this correlation the structure parameter Hammett equation employed is as shown in the following equation:

$$\nu = \rho\sigma + \nu_0 \quad \dots(1)$$

where ν is the carbonyl frequencies of substituted system and ν_0 is the corresponding quantity of unsubstituted system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent only and independent of the nature of reaction. ρ is a reaction constant is depends upon the nature of the reaction(temperature, solvent, catalyst and pressure).

The results of statistical analysis CN and NH stretching frequencies (ν , cm^{-1}) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines have been correlated with Hammett substituent constants and Swain-Lupton constants were shown in Table 3. From Table 3, the

inductive and field components were correlated satisfactorily with CN stretches of hydrazine derivatives (σ_I ; $r = 0.907$, F ; $r = 907$) The Hammett σ , σ^+ , σ_R substituent constants and R parameters were failing ($r < 0.900$) in correlation. This is due to the polar and resonance effects of the substituents are unable to predict the reactivity on the CN stretches and associated with the resonance conjugative structure as shown in Figure 1. All correlations show positive ρ values. This means that the normal substituent effect operates in all systems. Some of the single Hammett plots are shown in Figures 2 and 3.

Table 3. Results of statistical analysis of IR frequencies (ν , cm^{-1}) and NMR chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with Hammett substituent constants (σ , σ^+ , σ_I & σ_R) and F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
ν_{CN}	σ	0.810	1595.55	19.795	70.84	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.804	1596.83	25.397	71.18	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.907	1501.35	25.294	47.95	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_R	0.836	1570.72	92.736	66.21	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.907	1510.40	44.256	50.86	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.839	1657.37	89.403	65.58	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
ν_{NH}	σ	0.905	3276.90	12.846	7.88	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.905	3277.73	9.044	7.91	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.835	3271.81	15.781	8.66	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_R	0.836	3281.13	11.904	8.03	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.846	3270.38	18.533	8.22	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.832	3280.93	9.704	8.76	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
δ_{CH}	σ	0.905	8.702	0.130	0.07	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.901	8.771	0.077	0.07	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.892	8.711	0.077	0.07	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂

	σ_R	0813	8.690	0.056	0.08	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.844	8.747	0.120	0.08	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.826	8.679	0.080	0.08	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
δ_{NH}	σ	0.837	11.650	0.042	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.834	11.653	0.028	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.802	11.655	0.005	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_R	0.829	11.606	0.044	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.809	11.646	0.017	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.822	11.663	0.030	0.04	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
δ_{CH}	σ	0.975	147.78	3.376	1.09	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.975	148.00	3.246	1.18	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.824	147.25	2.015	1.63	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_R	0.872	149.14	4.001	1.24	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.827	147.22	1.988	1.62	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.926	149.15	3.492	1.28	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
δC_{ipso}	σ	0.888	149.00	3.577	15.32	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 4-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ^+	0.831	148.79	8.963	14.62	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_I	0.819	143.24	14.590	15.08	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	σ_R	0.834	143.53	18.517	14.14	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	F	0.841	137.99	26.98	14.07	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂
	R	0.836	142.58	18.942	14.21	9	H, 4-Br, 2-Cl,4-Cl, 4-F, 2-OH, 2-OCH ₃ , 4-OCH ₃ , 4NO ₂

r = correlation co-efficient; ρ = slope; I = intercept;
s = standard deviation; n = number of substituents.

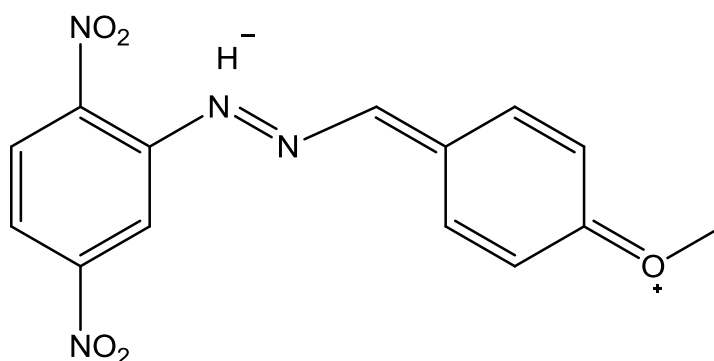


Figure 1. The resonance-conjugative structure.

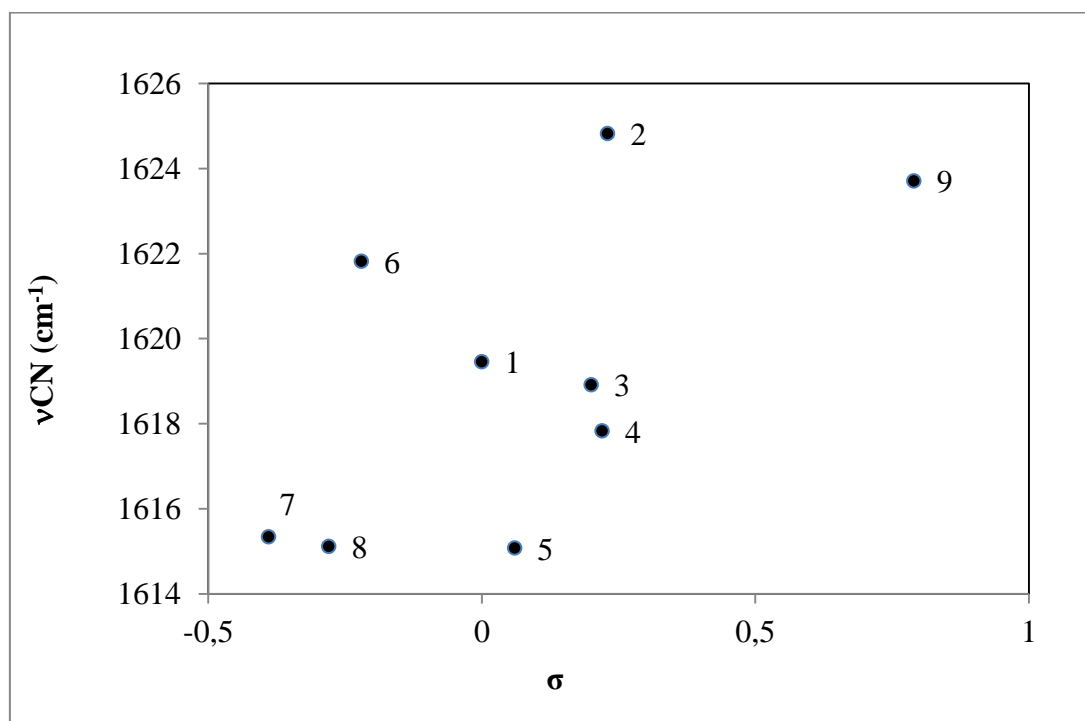


Figure 2. The plot of CN frequencies (ν , cm^{-1}) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

From table 3, the Hammett σ and σ^+ substituent constants were correlated satisfactorily with NH stretches (ν , cm^{-1}) of hydrazine derivatives (σ ; $r = 0.905$, σ^+ ; $r = 0.905$). The inductive, resonance and field effects of the substituents are failing ($r < 0.900$) in correlation. This is due to the inability of inductive, resonance and field effects to predict the reactivity on the NH stretches (ν , cm^{-1}) and associated with the resonance conjugative structure as shown in Figure 1. All correlations show positive ρ values. This means that the normal substituent effect operates in all systems. Some of the single Hammett plots are shown in Figures 4 and 5.

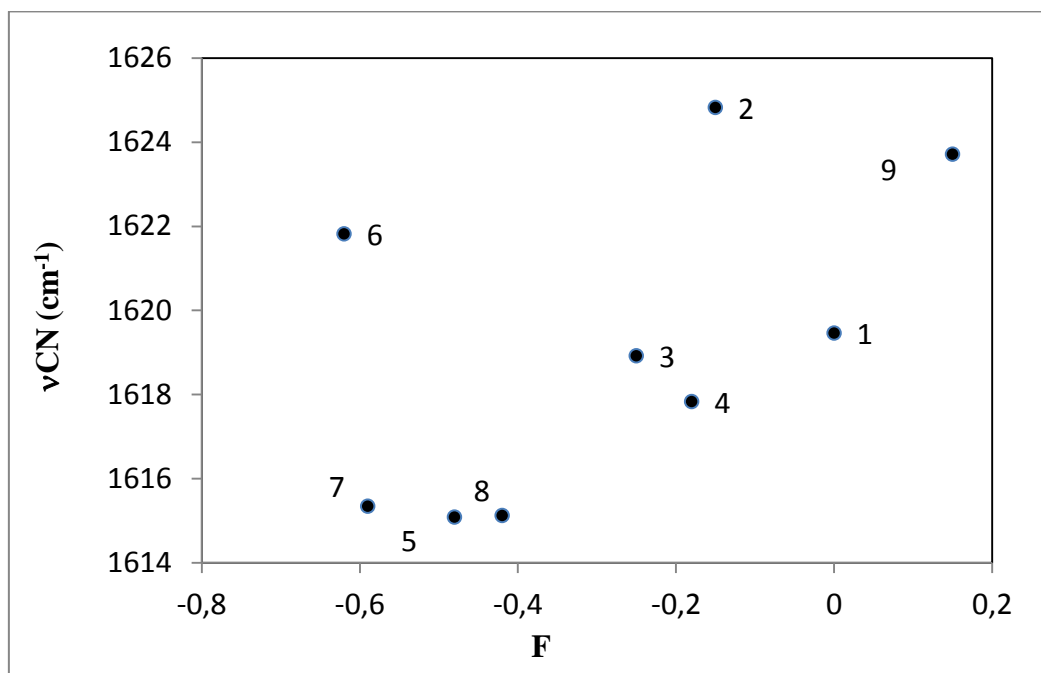


Figure 3. The plot of CN frequencies (ν , cm⁻¹) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with F parameter.

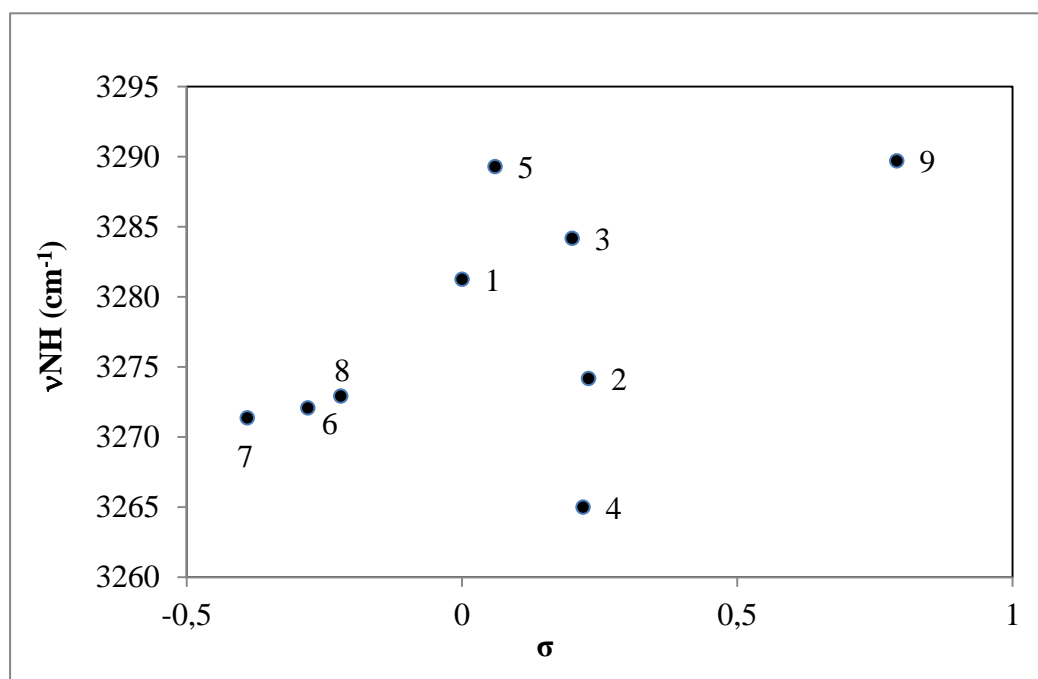


Figure 4. The plot of NH frequencies (ν , cm⁻¹) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

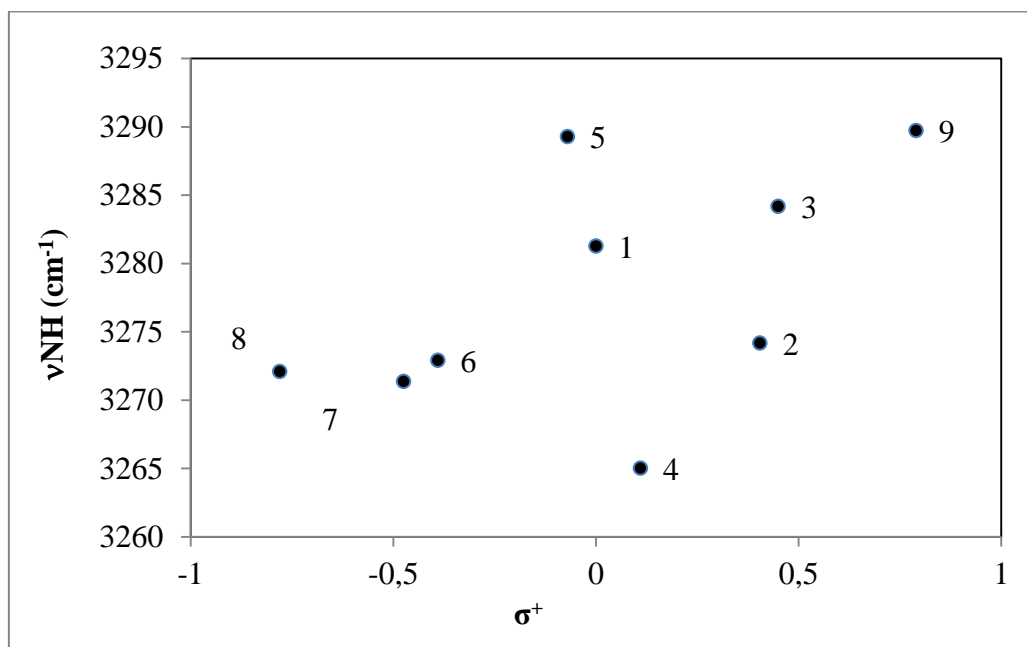


Figure 5. The plot of NH frequencies (ν , cm^{-1}) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ^+ constant.

Some of the single regressions of CN and NH stretching frequencies (ν , cm^{-1}) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are failure in correlations. These are worth full when seeking in multi-regression analysis [40]. The multi-regression analysis gave satisfactory correlations and the equations are given in (2-5).

$$\nu_{\text{CN}}(\text{cm}^{-1}) = 1447.11(\pm 28.971) + 293.00(57808)\sigma_{\text{I}} + 138.507(42.471)\sigma_{\text{R}} \quad \dots(2)$$

$(R = 0.992, n = 9, P > 95\%)$

$$\nu_{\text{CN}}(\text{cm}^{-1}) = 1485.48(\pm 38.984) + 211.95(\pm 78.010)F + 82.533(\pm 45.321)R \quad \dots(3)$$

$(R = 0.978, n = 9, P > 95\%)$

$$\nu_{\text{NH}}(\text{cm}^{-1}) = 3275.68(\pm 8.267) + 12.920(\pm 4.231)\sigma_{\text{I}} + 9.884(1.221)\sigma_{\text{R}} \quad \dots(4)$$

$(R = 0.946, n = 9, P > 95\%)$

$$\nu_{\text{NH}}(\text{cm}^{-1}) = 3273.49(\pm 6.725) + 19.145(\pm 3.457)F + 10.324(\pm 3.625)R \quad \dots(5)$$

$(R = 0.957, n = 9, P > 95\%)$

3. 2. NMR spectral correlations

3. 2. 1. ^1H NMR spectral study

From the ^1H NMR spectra CH and NH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are tabulated in Table 2. These chemical shifts (δ , ppm) were correlated with Hammett substituent constants and F and R parameters [38-40]. In these correlations, the Hammett equation was employed as in (6)

$$\delta = \rho\sigma + \delta_0 \quad \dots(6)$$

where δ is the carbonyl frequencies of substituted system and δ_0 is the corresponding quantity of unsubstituted system; σ is a Hammett substituent constant, which in principle is characteristics of the substituent only and independent of the nature of reaction. ρ is a reaction constant is depends upon the nature of the reaction(temperature, solvent, catalyst and pressure).

The statistical analysis of CH and NH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are presented in Table 3. The Hammett σ and σ^+ substituent constants were correlated satisfactorily with CH chemical shifts (δ , ppm) of hydrazine derivatives (σ ; $r = 0.975$, σ^+ ; $r = 975$). The inductive, resonance and field effects of the substituents are failing ($r < 0.900$) in correlation.

The NH chemical shifts (δ , ppm) of hydrazine derivatives were failed in correlation with Hammett substituent constants (σ , σ^+ , σ_I & σ_R) and *F* and *R* parameters ($r < 0.900$). This is due to the reasons stated earlier and associated with resonance-conjugative structure as shown in Figure 1. All correlations show positive ρ values. This means that the normal substituent effect operates in all systems. Some of the single Hammett plots are shown in Figures 6-9.

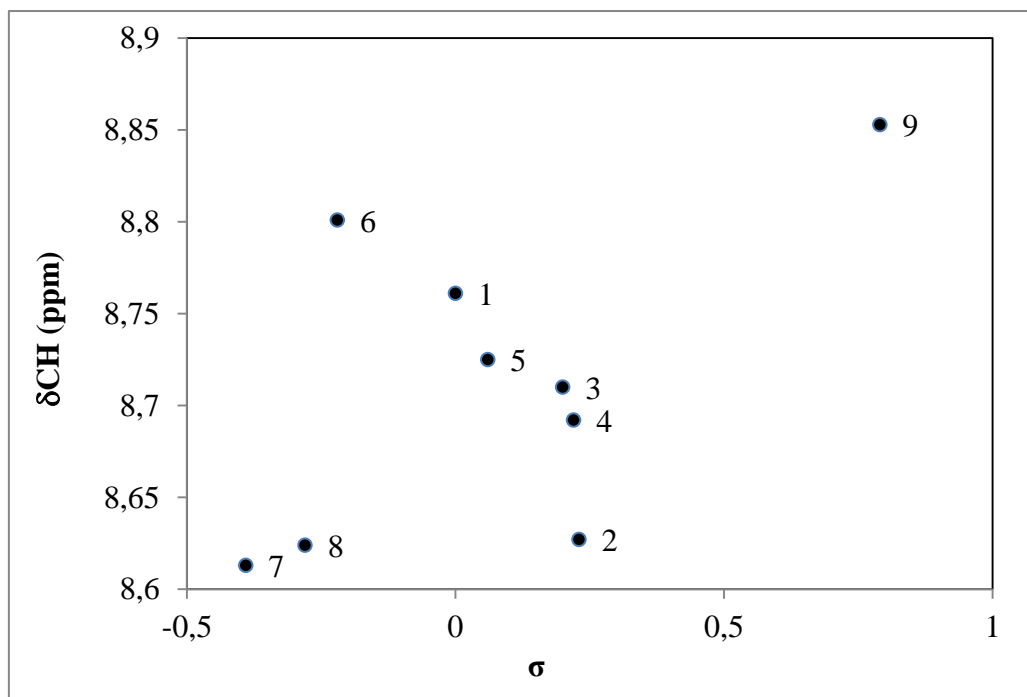


Figure 6. The plot of CH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

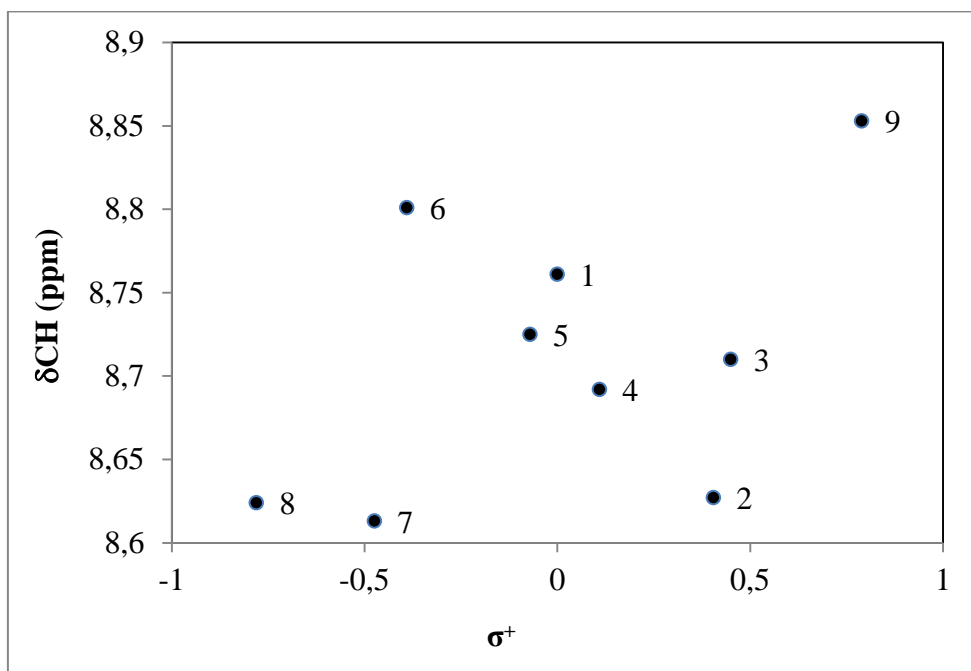


Figure 7. The plot of CH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ^+ constant.

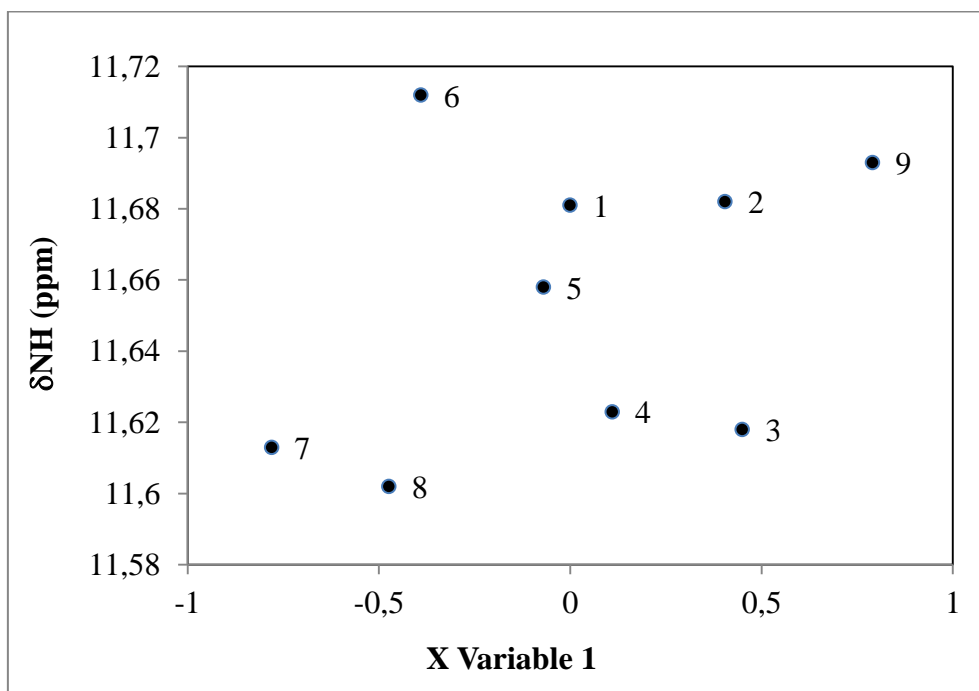


Figure 8. The plot of NH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

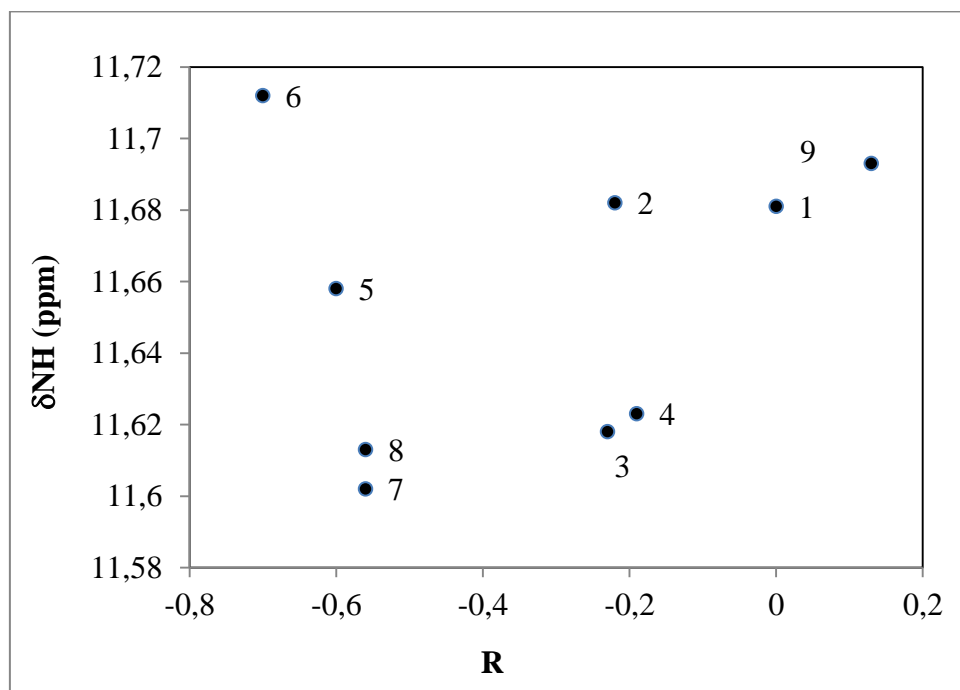


Figure 9. The plot of NH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ^+ constant.

Some of the single regressions of CN and NH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are failure in correlations. These are worth full when seeking in multi-regression analysis [40]. The multi-regression analysis gave satisfactory correlations and the equations are given in (7-10).

$$\delta\text{CH}(\text{ppm}) = 8.738(\pm 0.081) + 0.020(\pm 0.001)\sigma_{\text{I}} + 0.123(0.001)\sigma_{\text{R}} \quad \dots(7)$$

$(R = 0.940, n = 9, P > 90\%)$

$$\delta\text{CH}(\text{ppm}) = 8.713(\pm 0.070) + 0.086(\pm 0.014)F + 0.113(\pm 0.010)R \quad \dots(8)$$

$(R = 0.944, n = 9, P > 90\%)$

$$\delta\text{NH}(\text{ppm}) = 11.674(\pm 0.041) + 0.019(\pm 0.082)\sigma_{\text{I}} + 0.047(0.062)\sigma_{\text{R}} \quad \dots(9)$$

$(R = 0.930, n = 9, P > 90\%)$

$$\delta\text{NH}(\text{ppm}) = 11.656(\pm 0.037) + 0.019(\pm 0.074)F + 0.031(\pm 0.004)R \quad \dots(10)$$

$(R = 0.924, n = 9, P > 90\%)$

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

The statistical analysis of CH and C_{ipso} chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are presented in Table 3. The Hammett σ and σ^+ substituent constant and R parameters were correlated satisfactorily with CH chemical shifts (δ , ppm) of hydrazine derivatives (σ ; $r = 0.975$, σ^+ ; $r = 975$, R; $r = 0.926$). The inductive, resonance and field effects of the substituents are failing ($r < 0.900$) in correlation.

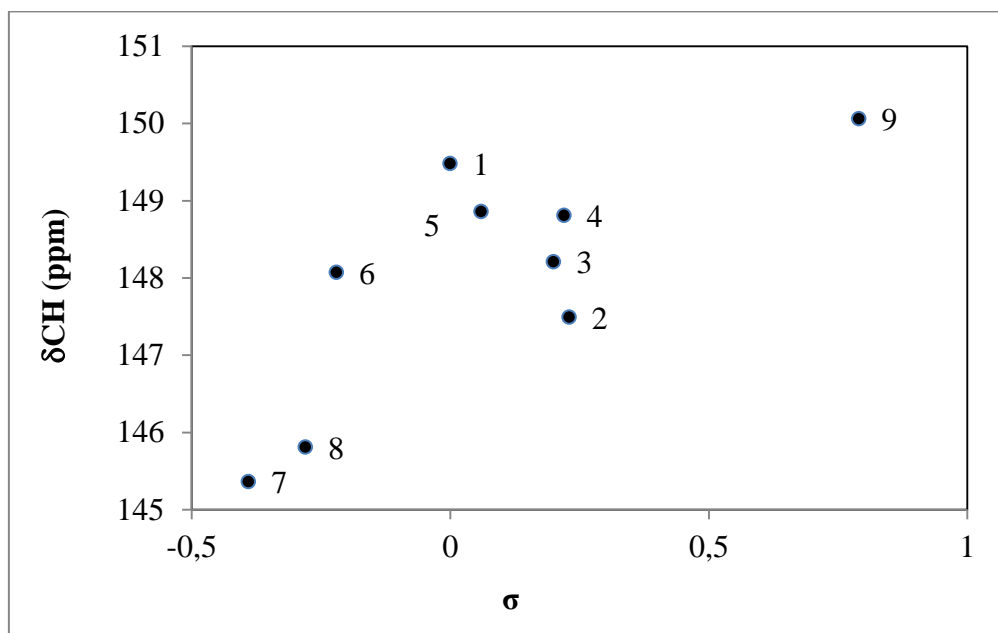


Figure 10. The plot of CH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

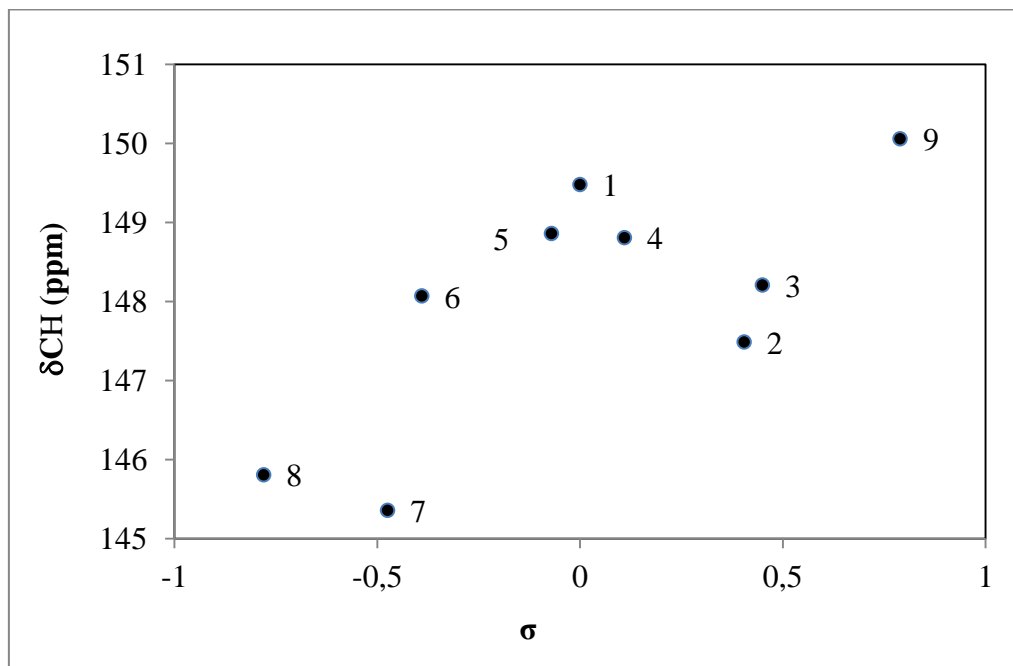


Figure 11. The plot of CH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ^+ constant

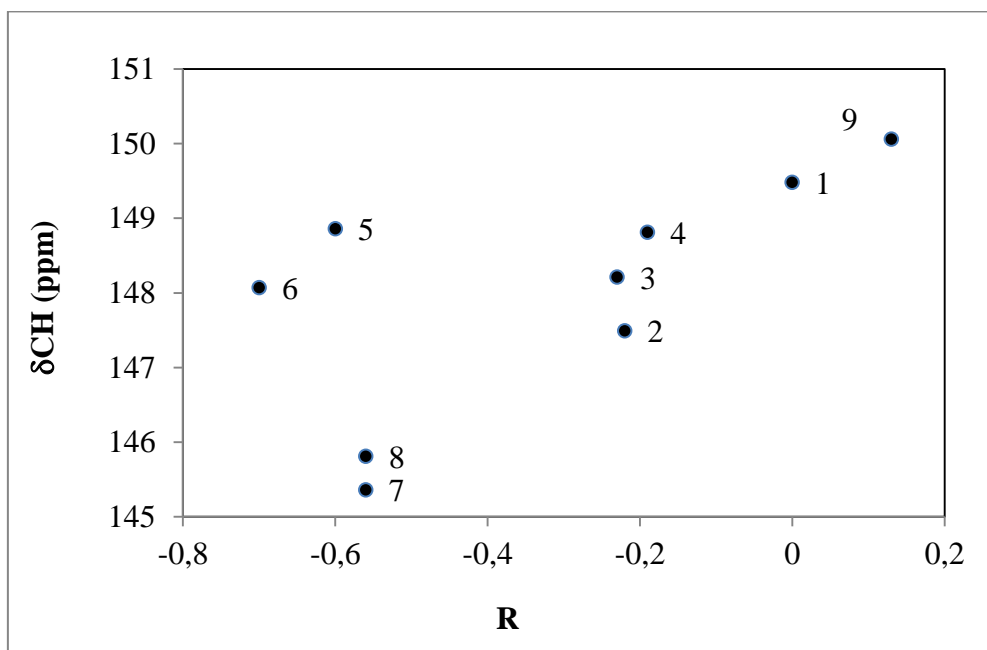


Figure 12. The plot of CH chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with R parameter.

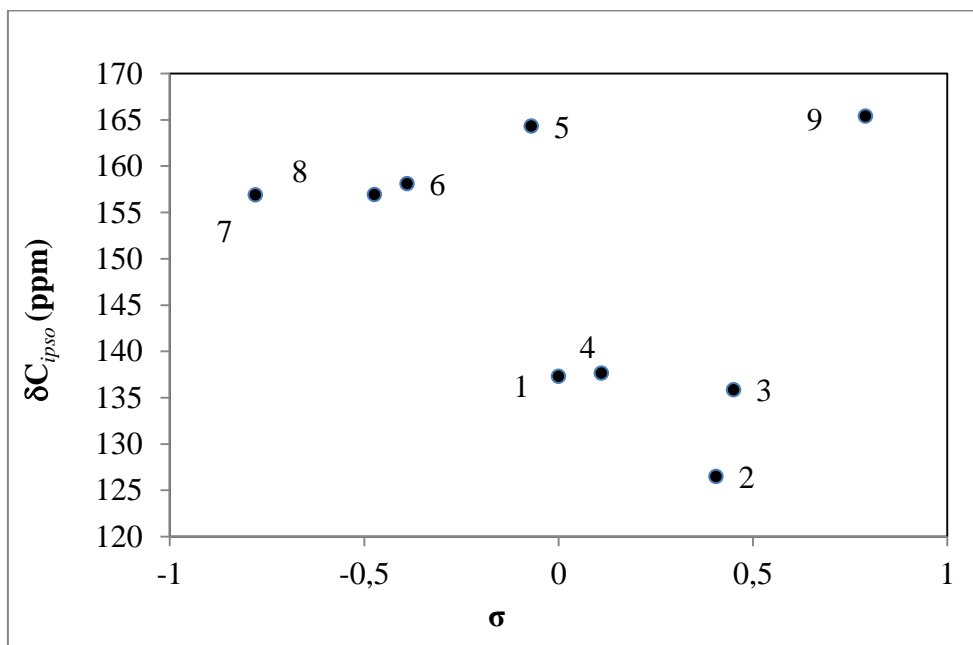


Figure 13. The plot of C_{ipso} chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ constant

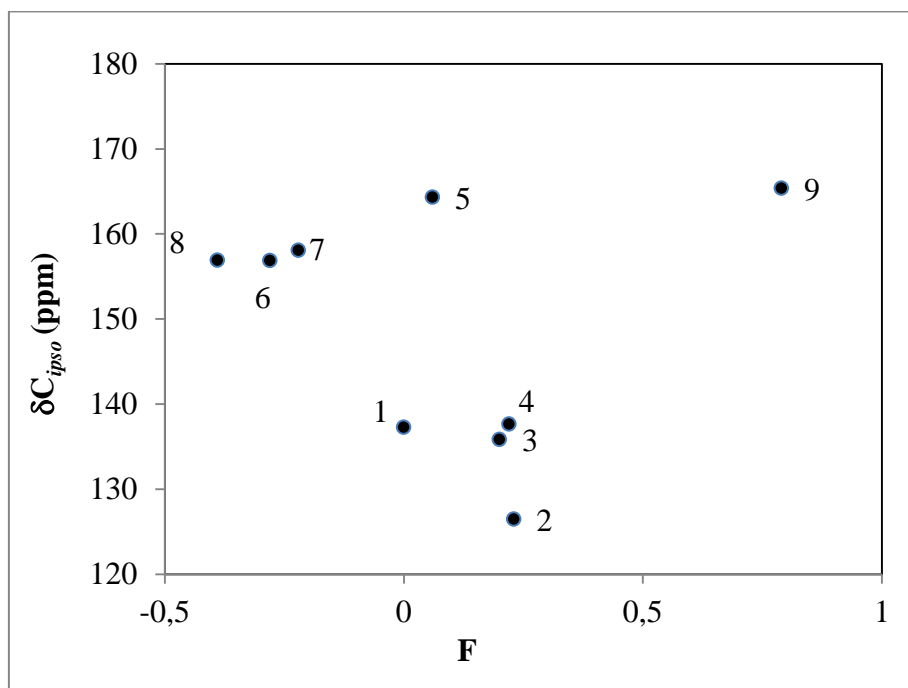


Figure 14. The plot of C_{ipso} chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines with σ^+ constant.

The C_{ipso} carbon chemical shifts (δ , ppm) of hydrazine derivatives were failed in correlation with Hammett substituent constants (σ , σ^+ , σ_I & σ_R) and F and R parameters ($r < 0.900$). This is due to the reasons stated earlier and associated with resonance-conjugative structure as shown in Figure 1. All correlations show positive ρ values. This means that the normal substituent effect operates in all systems. Some of the single Hammett plots are shown in Figures 10-14.

Some of the single regressions of CN and C_{ipso} carbon chemical shifts (δ , ppm) of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines are failure in correlations. These are worth full when seeking in multi-regression analysis [40]. The multi-regression analysis gave satisfactory correlations and the equations are given in (11-14).

$$\delta_{CH}(\text{ppm}) = 148.76(\pm 1.240) + 0.897(\pm 0.247)\sigma_I + 3.862(1.8191)\sigma_R \quad \dots(11)$$

$(R = 0.968, n = 9, P > 90\%)$

$$\delta_{CH}(\text{ppm}) = 148.29(\pm 1.052) + 2.200(\pm 0.021)F + 3.563(\pm 0.015)R \quad \dots(12)$$

$(R = 0.971, n = 9, P > 95\%)$

$$\delta_{C_{ipso}}(\text{ppm}) = 134.71(\pm 13.900) + 20.894(\pm 2.733)\sigma_I + 21.781(2.032)\sigma_R \quad \dots(13)$$

$(R = 0.943, n = 9, P > 90\%)$

$$\delta_{C_{ipso}}(\text{ppm}) = 132.52(\pm 11.452) + 25.912(\pm 2.291)F + 18.109(\pm 0.0163)R \quad \dots(14)$$

$(R = 0.954, n = 9, P > 90\%)$

3. 3. Antioxidant activity

The hydroxy- and methoxy- substituted organic compounds shows anti-oxidant activities. In this present investigation the authors measured the antioxidant activity of the synthesized hydrazine derivatives. The DPPH radical scavenging activity method [41] was employed for antioxidant measurements. About 20 mL of sodium acetate (0.1 M) solution was prepared by dissolving 1.64 g of sodium acetate in 15 mL of water and 150 μ L of acetic acid. About 50 mL of 0.2 mmol of DPPH solution was prepared by dissolving 3.9 g of DPPH in 50 mL of ethanol. About 10 mL of α -Tocopherol (1 mg in 10 mL of ethanol) solution was prepared.

About 1.0 mL of buffer and 0.5 mL of DPPH solution were added to the series of test tubes. All tubes were filled with various concentrations of synthesized epoxides and α -Tocopherol (1 μ g in 1 mL of ethanol) and mixed well. After 30 minutes, at room temperature, the absorbance of each solution is measured by UV-Vis spectrophotometer at 517 nm. Buffer solution and ethanol mixture was used as the reference for the spectrophotometer. The IC₅₀ values were determined from the plot of weight of the compound vs absorptions. The antioxidant activity was expressed in terms of IC₅₀ (μ g/mL, concentration required to inhibit DPPH radical formation by 50%). The α -Tocopherol was taken as a positive control. The measured antioxidant activities of hydrazine derivatives are presented in Table 4. From this experiment the hydrazines **6-8** were found to show antioxidant activity. Among these three compounds compound **6** shows significant antioxidant activity.

Table 4. Antioxidant activity of (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines

No	X	Antioxidant activity (DPPH radical scavenging)
1	H	22.15(\pm 1.35)
2	4-Br	19.32(\pm 1.71)
3	2-Cl	20.22(\pm 1.61)
4	4-Cl	20.25(\pm 1.26)
5	4-F	23.75(\pm 1.41)
6	4-OH	27.21(\pm 1.14)
7	2-OCH ₃	27.05(\pm 1.21)
8	4-OCH ₃	27.08(\pm 1.42)
9	4-NO ₂	17.05(\pm 1.86)
Standard		27.33(\pm 1.02)

4. CONCLUSIONS

Totally nine (*E*)-(2,5-dinitrophenyl)-2-(substituted benzylidene)hydrazines have been synthesized by hydroxy apatite catalyzed condensation of 2,4-dinitrophenyl hydrazine and substituted benzaldehydes under microwave irradiation conditions. The infrared spectral C=N, NH frequencies (ν , cm^{-1}) and the NMR spectral chemical shifts of CH, NH protons and carbons are assigned and are correlated with Hammett substituent constants, F and R parameter using single and multi-regression analysis. The inductive and field components were correlated satisfactorily with CN stretches of hydrazine derivatives (σ_I ; $r = 0.907$, F ; $r = 0.907$). The Hammett σ and σ^+ substituent constants were correlated satisfactorily with NH stretches (ν , cm^{-1}) of hydrazine derivatives (σ ; $r = 0.905$, σ^+ ; $r = 0.905$). The Hammett σ and σ^+ substituent constants were correlated satisfactorily with CH chemical shifts (δ , ppm) of hydrazine derivatives (σ ; $r = 0.975$, σ^+ ; $r = 0.975$). The NH chemical shifts (δ , ppm) of hydrazine derivatives were failed in correlation with Hammett substituent constants (σ , σ^+ , σ_I & σ_R) and F and R parameters ($r < 0.900$). The Hammett σ and σ^+ substituent constant and R parameters were correlated satisfactorily with CH chemical shifts (δ , ppm) of hydrazine derivatives (σ ; $r = 0.975$, σ^+ ; $r = 0.975$, R ; $r = 0.926$). All spectral frequencies are satisfactorily correlated with multi-regressions with Swain-Lupton's constants. The hydrazines **6-8** were found to show antioxidant activity. Among these three compounds compound **6** shows significant antioxidant activity.

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