

## Spectral correlations in some substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acids

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### ABSTRACT

A series of titled compounds were prepared and analyzed their purities by literature method. The infrared and NMR spectral group frequencies of the compounds were assigned and correlated with Hammett substituent constants, F and R constants using single and multi linear regression analysis. From the results of statistical analysis, the effect of substituents on the above spectral frequencies was discussed.

**Keywords:** Oxo-propyl diazenyl benzoic acid chalcones; IR spectra, NMR spectra, Hammett equation; Regression analysis

### 1. INTRODUCTION

Currently, scientists and chemists were paid more attention for utilizing the spectroscopic data for studying QSAR, QPR and QSR of organic molecules [1-10]. From these studies, the ground state configuration and the effect of substituents on the molecule have been evaluated [11]. Also the spectroscopic data were applied for predicting the behavior of electrochemical redox potential correlation [12], reaction transition state equilibrium [13], IC<sub>50</sub> value of drug molecule correlations [14], qualitative and quantitative estimation [15], enol-enone tautomerism [16]. Generally chalcones possess important biological activities such as anti-microbial [3], antidepressants [17], antiplosmodial [18], anti-aids [19] and insect antifeedant activities [20-22]. Infrared spectra is a good instrument for analyzing the structure of organic molecules [11], qualitative and quantitative measurements [15], geometrical isomers, *s-cis* and *s-trans* equilibration of unsaturated ketones, *anti*- and *gauche*- form of acyl compounds [1-10]. The NMR spectroscopic data were applied for predicting spatial arrangements of the *E* or *Z* isomers and conformers in unsaturated ketones, pyrazolines, *n*-acetyl pyrazoline, thiopyrazoline and its derivatives [6,7]. The effect of

substituents on the above molecular conformations also studied through Hammett substituent constants, F and R parameters [8]. Thirunarayanan have studied QSAR and QPR study with spectral frequencies in thiadiazole-2-amines [8]. Joseph and his co-workers have studied the effect of substituents on dimethyl phenyl chalcones by Hammett equation with spectral data [23]. Sekar and Thirunarayanan have evaluated the spectral correlation in pyrazoline derivatives [24]. The substituent effects on oxazine-2-amines were studied using spectral data using single and multi-regression analysis [25]. Kamalakkannan et al., have investigated the substituent effects on 2-indolyl chalcones by electrochemical redox potential with Hammett equation [26]. Kalyanasundaram et al., have studied the effect of substituents on phenoxyphenyl chalcones through IR and NMR spectroscopic data [10]. Within the above view there is no reported in the literature for the QSAR and QPR study of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acids in the past. Therefore the authors have taken efforts for studying the effect of substituent on the IR and NMR spectral data through Hammett equation using linear regression analysis.

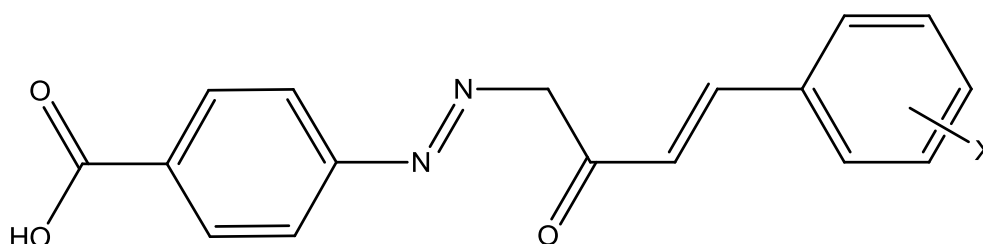
## 2. EXPERIMENTAL

### 2. 1. General

All chemicals and solvents used in this present study were purchased from Sigma-Aldrich and Merck companies. The infrared spectra of all chalcones were recorded in SHIMADUZ Fourier Transform IR spectrophotometer using KBr disc. The NMR spectra of all compounds have been recorded in BRUKER AV 400 type spectrometer, using CDCl<sub>3</sub> as a solvent, 400 MHz frequency was applied for recording <sup>1</sup>H, 100 MHz for <sup>13</sup>C NMR spectra, taking TMS as standard.

### 2. 2. Synthesis of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives.

The titled chalcones were prepared and their purities were analyzed by the literature method [27]. The general structure of the chalcones is illustrated in Fig. 1.



X= H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH<sub>3</sub>, 2-NO<sub>2</sub>, 4-NO<sub>2</sub>

**Fig. 1.** Structure of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acids. The analytical and spectroscopic data of selective compounds are given below.

**3-Bromostyryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid:** m.p. 143-144 °C, IR (KBr,  $\nu$ , 4000-400  $\text{cm}^{-1}$ ): 1715 ( $\text{CO}_{acid}$ ), 1686 ( $\text{CO}_{s-cis, keto}$ ), 1676 ( $\text{CO}_{s-trans, keto}$ ), 1483 (N=N); <sup>1</sup>HNMR ( $\delta$ , ppm): 6.514 (*d*, 1H, H <sub>$\alpha$</sub> ), 6.743 (*d*, 1H, H <sub>$\beta$</sub> ), 3.712 (*s*, 2H, CH<sub>2</sub>); <sup>13</sup>CNMR ( $\delta$ , ppm): 193.04

( $\text{CO}_{acid}$ ), 171.91 ( $\text{CO}_{keto}$ ), 124.01 ( $\text{C}_\alpha$ ), 143.02 ( $\text{C}_\beta$ ); M.F.  $\text{C}_{17}\text{H}_{13}\text{BrN}_2\text{O}_3$ ; M. W. 373; Mass (m/z): 373 [ $\text{M}^+$ ], 375 [ $\text{M}^{2+}$ ].

**4-Chlorostyryl (E)-4-((2-oxopropyl) diazenyl) benzoic acid:** m.p. 126-127 °C, IR (KBr,  $\nu$ , 4000-400  $\text{cm}^{-1}$ ): 1713 ( $\text{CO}_{acid}$ ), 1683 ( $\text{CO}_{s-cis, keto}$ ), 1662 ( $\text{CO}_{s-trans, keto}$ ), 1487 (N=N);  $^1\text{H}$  NMR ( $\delta$ , ppm): 6.361 (*d*, 1H,  $\text{H}_\alpha$ ), 6.517 (*d*, 1H,  $\text{H}_\beta$ ), 3.3.167 (*s*, 2H,  $\text{CH}_2$ );  $^{13}\text{C}$  NMR ( $\delta$ , ppm): 197.72 ( $\text{CO}_{acid}$ ), 170.97 ( $\text{CO}_{keto}$ ), 123.71 ( $\text{C}_\alpha$ ), 143.11 ( $\text{C}_\beta$ ); M. F.  $\text{C}_{17}\text{H}_{13}\text{ClN}_2\text{O}_3$ ; M. W. 329; Mass (m/z): 329 [ $\text{M}^+$ ], 331 [ $\text{M}^{2+}$ ].

### 3. RESULTS AND DISCUSSION

In the present investigations, the authors have studied the effect of substituents on the IR and NMR spectral group frequencies of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives using Hammett equation [1-12,23-29] with Hammett substituent constants and F and R parameters [30].

#### 3. 1. IR spectral study

The assigned  $\text{CO}_{acid}$ ,  $\text{CO}_{s-cis, keto}$ ,  $\text{CO}_{s-trans, keto}$  and N=N stretching frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) of prepared substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives were presented in Table 1.

**Table 1.** The IR and NMR spectroscopic data of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acids.

No.	X	IR ( $\nu$ , $\text{cm}^{-1}$ )				$^1\text{HNMR}$ ( $\delta$ , ppm)			$^{13}\text{CNMR}$ ( $\delta$ , ppm)			
		$\text{CO}_{acid}$	$\text{CO}_{s-cis, keto}$	$\text{CO}_{s-trans, keto}$	N=N	$\text{H}_\alpha$	$\text{H}_\beta$	$\text{CH}_2$	$\text{CO}_{acid}$	$\text{CO}_{s-cis, keto}$	$\text{C}_\alpha$	$\text{C}_\beta$
1	H	1713	1682	1668	1482	6.683	6.979	3.041	197.63	171.82	123.85	143.32
2	3-Br	1715	1686	1676	1483	6.514	6.743	3.172	197.04	171.91	124.01	143.02
3	2-Cl	1714	1690	1673	1484	6.481	6.881	3.092	198.03	171.17	124.93	143.14
4	4-Cl	1713	1683	1662	1487	6.361	6.517	3.167	197.72	170.97	123.71	143.11
5	2-OH	1711	1678	1654	1485	6.383	6.899	3.295	196.19	173.81	122.71	143.05
6	4-OH	1709	1687	1664	1483	6.493	6.871	3.151	198.09	175.77	123.81	142.75
7	4-OCH <sub>3</sub>	1710	1678	1660	1479	6.302	6.507	3.090	196.72	174.92	123.04	141.92

These data have been correlated with Hammett substituent constants and F and R parameter using linear regression analysis [1-12,23-29]. In Infrared spectral correlation, the Hammett equation is taken in the form of

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

where  $\nu_0$  is the frequency for the parent member of the series.

The results of statistical analysis [1-12,23-29] are presented in Table 2. From the Table 2, the  $\nu_{\text{CO}_{\text{acid}}}$  ( $\nu$ ,  $\text{cm}^{-1}$ ) frequencies correlated satisfactorily with Hammett substituent constants, F and R parameters. The correlation of  $\nu_{\text{CO}_{s\text{-cis keto}}}$  ( $\nu$ ,  $\text{cm}^{-1}$ ) frequencies were correlated satisfactorily. The Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_{\text{R}}$  constants and R parameters correlated satisfactorily for  $\nu_{\text{CO}_{s\text{-trans keto}}}$  ( $\nu$ ,  $\text{cm}^{-1}$ ) frequencies of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives. The Hammett  $\sigma_{\text{I}}$  constants and F parameter were fail in correlation with  $\nu_{\text{CO}_{s\text{-trans keto}}}$  ( $\nu$ ,  $\text{cm}^{-1}$ ) frequencies. This is due to the absence of inductive and polar effect of substituents on the carbonyl frequencies and is associated with the resonance conjugative structure as shown in Fig. 2.

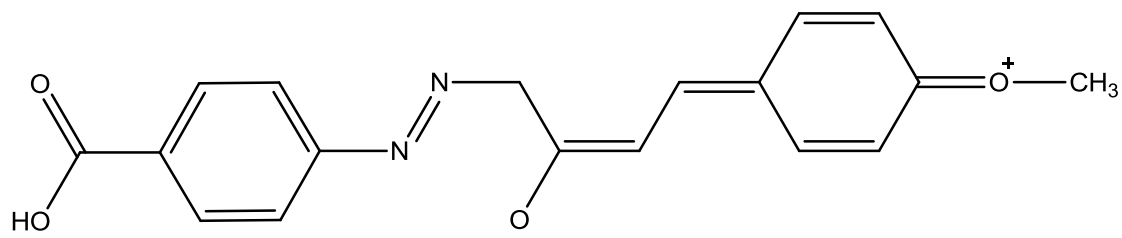


Fig. 2. The resonance and conjugative structure.

The  $\text{N}=\text{N}$  ( $\nu$ ,  $\text{cm}^{-1}$ ) stretching frequencies of all compounds correlated satisfactorily with Hammett  $\sigma$  constant and F parameter. The remaining Hammett  $\sigma^+$ ,  $\sigma_{\text{R}}$  and  $\sigma_{\text{I}}$  constants and R parameters were fail in correlations. The failure in correlation was due to the ineffective polar, inductive and resonance effect of substituents and associated with the resonance conjugative structure as shown in Fig. 2. All correlations gave positive  $\rho$  values. This means that the normal substituent effect operated in all systems.

Table 2. Results of statistical analysis of IR,  $^1\text{H}$  NMR and  $^{13}\text{C}$ -NMR spectral values of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acids with Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_{\text{I}}$ ,  $\sigma_{\text{R}}$  constants, F and R parameters.

Frequency	Constant	r	I	$\rho$	s	n	Correlated derivatives
$\nu_{\text{CO}_{\text{acid}}}$ ( $\text{cm}^{-1}$ )	$\sigma$	0.906	1712.79	4.617	2.55	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.905	1713.44	2.919	2.67		
	$\sigma_{\text{I}}$	0.902	1710.58	7.681	2.80		
	$\sigma_{\text{R}}$	0.905	1714.89	6.841	2.46		
	F	0.915	1710.39	8.043	2.41		
	R	0.919	1714.83	4.900	2.40		
$\nu_{\text{CO}_{s\text{-cis keto}}}$ ( $\text{cm}^{-1}$ )	$\sigma$	0.971	1683.71	9.823	3.82	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.970	1685.08	6.210	4.10		
	$\sigma_{\text{I}}$	0.973	1677.94	19.118	3.96		
	$\sigma_{\text{R}}$	0.968	1688.08	14.051	4.25		
	F	0.969	1677.77	19.205	4.23		
	R	0.962	1688.77	10.544	4.54		
$\nu_{\text{CO}_{s\text{-trans keto}}}$ ( $\text{cm}^{-1}$ )	$\sigma$	0.958	1664.46	9.342	5.87	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.964	1665.71	9.066	5.51		
	$\sigma_{\text{I}}$	0.838	1661.26	12.240	7.15		
	$\sigma_{\text{R}}$	0.962	1669.05	15.820	5.63		

	F	0.823	1662.63	8.532	7.00		
	R	0.963	1669.26	12.564	5.74		
$\nu_{N=N}$ ( $\text{cm}^{-1}$ )	$\sigma$	0.957	1496.87	140.092	88.87	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.744	1515.51	73.502	97.63		
	$\sigma_I$	0.848	1427.51	234.024	95.46		
	$\sigma_R$	0.849	1554.89	188.642	94.80		
	F	0.905	1414.96	261.942	89.23		
	R	0.817	1436.21	142.815	96.74		
$\delta_{H\alpha}$ (ppm)	$\sigma$	0.917	6.483	0.332	0.13	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.916	6.529	0.207	0.15		
	$\sigma_I$	0.838	6.403	0.348	0.18		
	$\sigma_R$	0.928	6.656	0.107	0.10		
	F	0.837	6.394	0.364	0.18		
	R	0.976	6.657	0.461	0.12		
$\delta_{H\beta}$ (ppm)	$\sigma$	0.848	6.803	0.256	0.20	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.849	6.831	0.177	0.20		
	$\sigma_I$	0.822	6.751	0.237	0.23		
	$\sigma_R$	0.905	6.927	0.421	0.20		
	F	0.828	6.721	0.314	0.22		
	R	0.848	6.931	0.325	0.20		
$\delta_{CH_2}$ (ppm)	$\sigma$	0.718	3.148	0.020	0.17	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.805	3.152	0.071	0.04		
	$\sigma_I$	0.834	3.105	0.117	0.02		
	$\sigma_R$	0.827	3.137	0.075	0.03		
	F	0.486	3.081	0.181	0.16		
	R	0.725	3.137	0.075	0.16		
$\delta_{CO_{acid}}$ (ppm)	$\sigma$	0.841	197.36	0.664	0.64	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.831	197.45	0.418	0.65		
	$\sigma_I$	0.736	197.03	1.171	0.66		
	$\sigma_R$	0.905	197.76	1.495	0.57		
	F	0.817	196.17	1.131	0.63		
	R	0.900	198.13	2.714	0.59		
$\delta_{CO_{keto}}$ (ppm)	$\sigma$	0.671	173.49	0.388	2.23	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.717	173.58	0.640	2.21		
	$\sigma_I$	0.725	172.99	2.501	2.17		
	$\sigma_R$	0.716	173.66	0.513	2.24		
	F	0.840	171.84	4.291	2.05		
	R	0.808	173.41	5.631	2.20		
$\delta_{C\alpha}$ (ppm)	$\sigma$	0.718	123.60	0.170	0.70	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.728	123.62	0.311	0.68		
	$\sigma_I$	0.707	123.54	0.747	0.70		
	$\sigma_R$	0.718	132.75	0.464	0.69		

	F	0.769	123.77	0.231	0.52		
	R	0.822	123.75	0.454	0.50		
$\delta C\beta$ (ppm)	$\sigma$	0.981	142.93	1.155	0.37	9	H, 3-Br, 2-Cl, 4-Cl, 2-OH, 4-OH, 4-OCH <sub>3</sub> , 2-NO <sub>2</sub> , 4-NO <sub>2</sub>
	$\sigma^+$	0.982	142.93	1.791	0.36		
	$\sigma_I$	0.905	142.55	1.544	0.54		
	$\sigma_R$	0.971	143.45	1.968	0.42		
	F	0.905	142.52	1.527	0.55		
	R	0.977	143.49	1.421	0.40		

R = correlation coefficient; I = intercept;  $\rho$  = slope; s = standard deviation; n = number of correlated derivatives

Some of the single linear regressions were fail for  $CO_{s-trans\ keto}$  and  $N=N$  ( $\nu$ ,  $cm^{-1}$ ) stretching frequencies of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives. While seeking the multi-regression analysis of the infrared group frequencies, they were satisfactorily correlated with  $\sigma_I$  and  $\sigma_R$  constants and F and R Swain Lupton's [30] constants. The generated multi-regression analysis equations are given in (2-9).

$$\nu CO_{acid}(cm^{-1}) = 1712.81(\pm 2.675) + 4.486(\pm 0.522)\sigma_I + 5.088(\pm 0.411)\sigma_R \quad \dots(2)$$

$(R = 0.965, n = 9, P > 95 \%)$

$$\nu CO_{acid}(cm^{-1}) = 1712.19(\pm 2.712) + 5.832(\pm 0.537)F + 3.611(\pm 0.323)R \quad \dots(3)$$

$(R = 0.962, n = 9, P > 95 \%)$

$$\nu CO_{s-cis\ keto}(cm^{-1}) = 1681.78(\pm 3.536) + 13.639(\pm 6.906)\sigma_I + 13.639(\pm 6.906)\sigma_R \quad \dots(4)$$

$(R = 0.965, n = 9, P > 95 \%)$

$$\nu CO_{s-cis\ keto}(cm^{-1}) = 1681.42(\pm 36.995) + 14.751(\pm 7.330)F + 7.278(\pm 4.412)R \quad \dots(5)$$

$(R = 0.979, n = 9, P > 95 \%)$

$$\nu CO_{s-trans\ keto}(cm^{-1}) = 1667.68(\pm 5.983) + 3.051(\pm 1.683)\sigma_I + 14.624(\pm 1.963)\sigma_R \quad \dots(6)$$

$(R = 0.963, n = 9, P > 95 \%)$

$$\nu CO_{s-cis\ keto}(cm^{-1}) = 1668.81(\pm 6.039) + 0.999(\pm 0.111)F + 12.342(\pm 1.721)R \quad \dots(7)$$

$(R = 0.960, n = 9, P > 95 \%)$

$$\nu N=N(cm^{-1}) = 1483.98(\pm 95.954) + 153.112(\pm 18.735)\sigma_I + 128.816(\pm 14.714)\sigma_R \quad \dots(8)$$

$(R = 0.956, n = 9, P > 95 \%)$

$$\nu NH_2(cm^{-1}) = 1464.18(\pm 93.181) + 201.78(\pm 18.481)F + 198.297(\pm 11.174)R \quad \dots(9)$$

$(R = 0.958, n = 9, P > 95 \%)$

### 3. 2. NMR spectral study

In nuclear magnetic resonance spectra, the  $^1\text{H}$  or the  $^{13}\text{C}$  chemical shifts ( $\delta$ , ppm) depend on the electronic environment of the nuclei concerned. These chemical shifts of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives have been correlated with reactivity parameters. Thus the Hammett equation was used in the form as shown in (10).

$$\text{Log } \delta = \text{Log } \delta_0 + \rho\sigma \quad \dots (10)$$

where  $\delta_0$  is the chemical shift of the corresponding parent compound.

#### 3. 2. 1. $^1\text{H}$ NMR spectral study

The  $^1\text{H}$  NMR spectra of these synthesized substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives under investigations were recorded in deuteriochloroform solution using tetramethylsilane (TMS) as internal standard. The chemical shifts of ( $\delta$ , ppm) vinyl protons of these compounds have been assigned and tabulated in Table 1. The results of statistical analysis [1-12,23-29] were presented in Table 2. From the Table 2, the correlation of  $\text{H}\alpha$  chemical shifts ( $\delta$ , ppm) of the chalcones were satisfactory for Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$  constants and R parameter.

The Hammett  $\sigma_I$  constant and F parameter were fail in correlation for these chemical shifts. Only the Hammett  $\sigma_R$  constant gave satisfactory correlation with  $\text{H}\beta$  chemical shifts ( $\delta$ , ppm) of the chalcones. The remaining Hammett substituent constants, F and R parameters were fail in correlations. This is due to the inability of effect of substituents on the vinyl protons of the chalcones and is associated with the resonance conjugative structure as shown in Fig. 2. The correlation of methylene protons ( $\delta$ , ppm) of the chalcones were fail in correlation with Hammett substituent constants and F and R parameters. The reason for failure in correlation was stated earlier and it is associated with the resonance conjugative structure as shown in Fig. 2. All correlations gave positive  $\rho$  values. This means that the normal substituent effect operated in all systems.

Some of the single parameter correlations were fail for vinyl and methylene proton chemical shifts ( $\delta$ , ppm) of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives. While seeking the multi-regression analysis, these chemical shifts ( $\delta$ , ppm) were satisfactorily correlated with  $\sigma_I$  and  $\sigma_R$  constants and F and R Swain Lupton's [30] constants. The generated multi-regression analysis equations are given in (11-16).

$$\delta\text{H}\alpha(\text{ppm}) = 6.676(\pm 0.113) - 0.042(\pm 0.021)\sigma_I + 0.622(\pm 0.175)\sigma_R \quad \dots(11)$$

$(R = 0.985, n = 9, P > 95 \%)$

$$\delta\text{H}\alpha(\text{ppm}) = 6.614(\pm 0.129) + 0.095(\pm 0.025)F + 0.440(\pm 0.154)R \quad \dots(12)$$

$(R = 0.979, n = 9, P > 95 \%)$

$$\delta\text{H}\beta(\text{ppm}) = 6.944(\pm 0.217) + 0.036(\pm 0.004)\sigma_I + 0.435(\pm 0.033)\sigma_R \quad \dots(13)$$

$(R = 0.951, n = 9, P > 95 \%)$

$$\delta\text{H}\beta(\text{ppm}) = 6.869(\pm 0.216) + 0.133(\pm 0.042)F + 0.295(\pm 0.021)R \quad \dots(14)$$

$(R = 0.949, n = 9, P > 90 \%)$

$$\delta\text{CH}_2(\text{ppm}) = 3.034(\pm 0.062) + 0.221(\pm 0.128)\sigma_I + 0.162(\pm 0.011)\sigma_R \quad \dots(15)$$

$$(R = 0.961, n = 9, P > 95 \%)$$

$$\delta\text{CH}_2(\text{ppm}) = 3.024(\pm 0.060) + 0.250(\pm 0.120)F + 0.113(\pm 0.072)R \quad \dots(16)$$

$$(R = 0.967, n = 9, P > 95 \%)$$

### 3. 2. 2. $^{13}\text{C}$ NMR spectra

In the present study, the chemical shifts ( $\delta$ , ppm) of  $\text{CO}_{acid, keto}$  and vinyl carbons of the synthesized chalcones derivatives have been assigned and are presented in Table 1. Attempts have been made to correlate the above said carbon chemical shifts ( $\delta$ , ppm) with Hammett substituent constants, field and resonance parameters with the help of single and multi-regression analyses to study the reactivity through the effect of substituents. The results of statistical analysis [1-12,23-29] are presented in Table 2. The  $\delta\text{CO}_{acid}$  chemical shifts (ppm) gave satisfactory correlations with Hammett  $\sigma_R$  substituent constants, R parameter. The remaining Hammett substituent constants and F parameters were fail in correlation. The correlation of  $\delta\text{CO}_{acid}$  and  $\delta\text{C}\alpha$  chemical shifts ( $\delta$ , ppm) was fail in correlation for Hammett substituent constants and F and R parameters. The reason for failure in correlation was stated already and is associated with resonance conjugative structure as shown in Fig. 2. The  $\delta\text{C}\beta$  chemical shifts ( $\delta$ , ppm) of all ketones were satisfactorily correlated with Hammett substituent constants and F and R parameters. All correlations gave positive  $\rho$  values. This means that the normal substituent effect operates in all systems.

Some of the single parameter correlations were fail for  $\text{CO}_{acid, keto}$  and vinyl carbons chemical shifts ( $\delta$ , ppm) of substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives. While seeking the multi-regression analysis, these chemical shifts ( $\delta$ , ppm) were satisfactorily correlated with  $\sigma_I$  and  $\sigma_R$  constants and F and R Swain Lupton's [30] constants. The generated multi-regression analysis equations are given in (17-24).

$$\delta\text{CO}_{acid}(\text{ppm}) = 197.61(\pm 0.635) + 2.971(\pm 1.261)\sigma_I + 1.014(\pm 0.075)\sigma_R \quad \dots(17)$$

$$(R = 0.953, n = 9, P > 95 \%)$$

$$\delta\text{CO}_{acid}(\text{ppm}) = 197.64(\pm 0.608) + 0.270(\pm 0.118)F + 1.383(\pm 0.093)R \quad \dots(18)$$

$$(R = 0.960, n = 9, P > 95 \%)$$

$$\delta\text{CO}_{keto}(\text{ppm}) = 172.32(\pm 2.313) + 2.886(\pm 0.415)\sigma_I + 6.123(\pm 2.3175)\sigma_R \quad \dots(19)$$

$$(R = 0.926, n = 9, P > 90 \%)$$

$$\delta\text{CO}_{keto}(\text{ppm}) = 170.99(\pm 2.079) + 5.367(\pm 0.413)F + 1.757(\pm 0.248)R \quad \dots(20)$$

$$(R = 0.947, n = 9, P > 90 \%)$$

$$\delta\text{C}\alpha(\text{ppm}) = 123.75(\pm 0.745) - 0.058(\pm 0.004)\sigma_I + 0.478(\pm 0.114)\sigma_R \quad \dots(21)$$

$$(R = 0.918, n = 9, P > 90 \%)$$

$$\delta\text{C}\alpha(\text{ppm}) = 124.02(\pm 0.719) - 0.590(\pm 0.412)F + 0.585(\pm 0.085)R \quad \dots(22)$$

$$(R = 0.947, n = 9, P > 90 \%)$$

$$\delta\text{C}\beta(\text{ppm}) = 143.20(\pm 0.434) + 0.544(\pm 0.084)\sigma_I + 1.479(\pm 0.665)\sigma_R \quad \dots(23)$$

$$(R = 0.977, n = 9, P > 90 \%)$$



$$\delta C\beta(\text{ppm}) = 143.15(\pm 0.396) + 0.760(\pm 0.078)F + 1.255(\pm 0.475)R \quad \dots(24)$$

$(R = 0.980, n = 9, P > 95 \%)$

#### 4. CONCLUSIONS

A series containing nine substituted styryl (*E*)-4-((2-oxopropyl) diazenyl) benzoic acid derivatives were prepared and analyzed their purities by reported method. The infrared  $\text{CO}_{acid}$ ,  $\text{CO}_{s-cis, keto}$ ,  $\text{CO}_{s-trans, keto}$  and  $\text{N}=\text{N}$  stretching frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ),  $^1\text{H}$  chemical shifts ( $\delta$ , ppm) of vinyl, methylene protons,  $^{13}\text{C}$  chemical shifts ( $\delta$ , ppm) of  $\text{CO}_{acid}$ ,  $\text{CO}_{keto}$  and vinyl carbons were assigned and correlated with Hammett substituent constants and F and R parameters. The infrared  $\text{CO}_{acid}$ ,  $\text{CO}_{s-cis, keto}$  stretching frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) were correlated satisfactorily. The  $\text{CO}_{s-trans, keto}$  stretching frequencies ( $\nu$ ,  $\text{cm}^{-1}$ ) were correlated satisfactorily for Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$  constants and R parameters. The  $^1\text{H}$  chemical shifts of  $\text{H}\alpha$  ( $\delta$ , ppm) of vinyl protons were satisfactorily correlated with Hammett  $\sigma$ ,  $\sigma^+$ ,  $\sigma_R$  constants and R parameters. The  $\text{H}\beta$  ( $\delta$ , ppm) of vinyl protons were satisfactorily correlated only with Hammett  $\sigma_R$  constant. The  $^{13}\text{C}$  chemical shifts ( $\delta$ , ppm) of  $\text{CO}_{acid}$  carbons were satisfactorily correlated with Hammett  $\sigma_R$  constants and R parameters. The vinyl  $\text{C}\beta$  ( $\delta$ , ppm) carbon chemical shifts of prepared compounds were satisfactorily correlated with Hammett substituent constants, F and R parameters.

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