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Infrared and ^{13}C NMR Spectral Correlation Analysis of Some Substituted Oxazepin Based Ketone and Thione Derivatives with Hammett Constant

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ABSTRACT

Single and multi-regression analysis was applied for the corrosion study of transmission of substituent effects on IR carbonyl stretching frequencies and ^{13}C chemical shifts of some substituted oxazepin compounds. The substituent effects were estimated on the basis of results of the statistical analysis. The differences among the obtained regression coefficients were discussed in terms of the relative importance of the field, inductive and resonance effects of substituent.

***Keywords*:** Oxazepins; IR; ^{13}C NMR; Hammett constant; F and R parameter; Single and multi-regression analysis

1. INDRODUCTION

The QSAR study of physical organic chemistry is to explain and correlates [1-3] the empirical facts of chemistry. Hammett's success in treating the electronic effect of substituents on the rates and equilibria of organic reactions [4-5] led Taft [6] to apply the same principles to steric and inductive and resonance effects. One of the more useful generalizations of physical organic chemistry is the Hammett [7] equation. This equation correlates the rates of over two hundred reactions with the structure of the reactants. The equation as it stands now is applicable only to reactions of aromatic compounds and their derivatives. Hammett constants have been extremely effective in describing the influence of substituents on chemical reactivity and other physical and chemical properties, Hammett constants (σ) have been the workhorse of organic chemists in relating the nature of substituents to their effects on chemical reactivity and other properties. These constants remains today an excellent guide in structure property and structure-activity studies. In a recent review Hansch observed [8], Hammett constants have been astonishingly successful in correlating almost every kind of organic reaction in all sorts of solvents.

Infrared (IR) spectroscopy is a powerful tool for the qualitative and quantitative study of natural and synthetic molecules [9]. IR spectroscopy can provide information about the nature, concentration and structure of samples at the molecular levels. It is well demonstrated in the literature [10,11] that infrared (IR) stretching frequencies are sensitive probes of electron-density distributions and are useful for studies on the transmission of electronic effects in organic molecules. Recently, several physical properties concerning the C=O and C=S groups have been published for a great number of organic structures. Especially, infrared carbonyl stretching frequencies of many organic compounds were measured under nearly standard conditions[12], *i.e.* in dilute solutions of CCl_4. Most of these compounds contained complex substituents or structural fragments attached to the C=O and C=S groups.

In order to examine the applicability of the improved Seth-Paul Van Duyse equation [13] to the C=O stretching frequencies of further organic compounds, the main goal of the present work was to derive an empirical equation for calculation of substituent constants of complex structural fragments and determine or collect several trans-missive factors and substituent constants necessary for this calculations. In the present investigations, the authors have evaluated the substituent effects on infrared C=O, C-O-C and C=S vibrations (ν, cm^{-1}) and ^{13}C NMR spectral chemical shifts (δ, ppm) of CO, CS, CN and ipso carbons of some oxazapine derivatives.

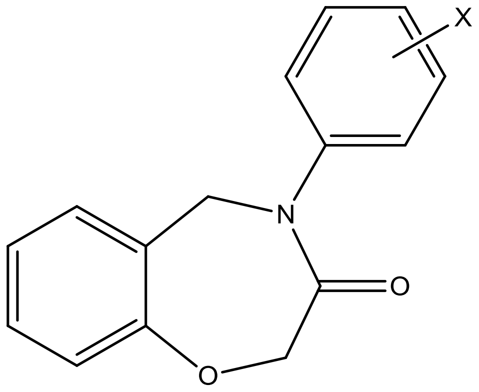
2. EXPERIMENTAL

2. 1. General

In this present work, all chemicals used were purchased from Sigma-Aldrich Company Bangalore, India. Melting points were determined using Mettler FP51 melting-point apparatus and are uncorrected. Infrared spectra (KBr, 4000-400 cm^{-1}) were recorded on a Briker (Thermo Nicolet) Fourier transform spectrophotometer. The NMR spectra of all oxazepin derivatives were recorded on a Bruker AV400 spectrometer operating at 100 MHz for ^{13}C spectra in $CDCl_3$ solvent with TMS as internal standard

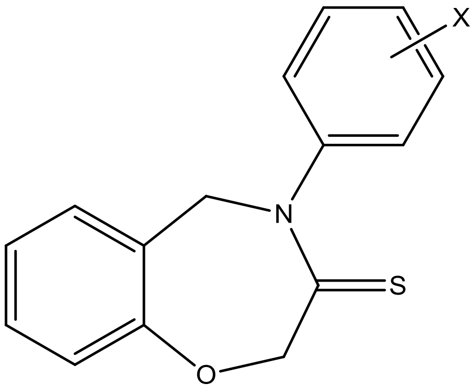
2. 2. Synthesis of oxazepin derivative

Oxazepin derivatives were synthesized according to the literature [14]. The general structure of synthesized compounds are shown in Figures 1 and 2. For the synthesis of compounds, literature methods [15-17] were applied some modifications



X= H, 4-Br, 3-Cl, 4-Cl, 4-N$(CH_3)_2$, 4-F, 4-I, 3-O CH_3, 4-O CH_3, 3- CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 3-CF_3

Fig. 1. Substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones



X= H, 4-Br, 3-Cl, 4-Cl, 4-N$(CH_3)_2$, 4-F, 4-I, 3-O CH_3, 4-O CH_3, 3- CH_3, 4-CH_3, 3-NO_2, 4-NO_2, 3-CF_3

Fig. 2. Substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones

3. RESULTS AND DISCUSSION

3. 1. Correlation analysis of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones

The assigned infrared stretches (ν, cm^{-1}) and ^{13}C NMR chemical shifts (δ, ppm) of synthesized oxazepin derivatives were shown in Table 1. These infrared spectral data of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-one, the characteristic stretching frequencies (ν, cm^{-1}) of C=O and C-O-C, ^{13}C spectra chemical shifts values of (δ, ppm) of CO, N-Ar and ipso carbon are correlated with Hammett constant and F and R parameters [18-25]. In the infrared correlations, the Hammett equation was employed as (1) and the ^{13}C NMR correlations this equation taken as (2).

$$\nu = \rho\sigma + \nu_0 \qquad \ldots (1)$$

where: ν_0 is the carbonyl frequencies of unsubstituted system

$$\delta \ = \rho\sigma + \delta \qquad \ldots (2)$$

where: δ_0 is the chemical shifts (ppm) of particular nuclei of unsubstituted system.

The results of statistical analysis are shown in the Table 2. From the Table 2, compounds containing the carbonyl group present a strong absorption band in the infrared region The stretching frequencies of C=O (1653.15-1676.74) gives good correlation with all the Hammett constants and F and R parameters, this shown more electron negativity of the oxygen atom involve the polar, inductive, resonance and field effect. All the single linear correlation has shown ($r > 0.900$) higher correlation-coefficient value, σ^+ ($r = 0.968$), σ_I ($r = 0.965$). Another stretching frequency of υC-O-C (1221.8-1269 cm^{-1}) shown satisfactory correlation, especially σ_I ($r = 0.978$) have shown high correlation coefficient. Its indicate high inductive effect operate υC-O-C stretching frequency with all substituents. All the correlation has shown positive ρ value for IR stretching frequencies of C=O and C-O-C (υ, cm^{-1}) spectral data. It is equivalent to the slope of the Hammett plot. Information on the reaction, including that related to mechanism can be obtained based on the value of ρ. If the value ($\rho > 1$) the reaction is more sensitive to substituents

The ^{13}C NMR chemical shift values of CO (166.21-170.74 δ, ppm) in all the substituent with Hammett constant and Swain-Lupton parameters [26] have shown satisfactory correlation, σ ($r = 0.981$), σ+ ($r = 0.968$) gives high correlation coefficient value because δC=O has more polar effect with all the substituent and σ_I ($r = 0.976$) reveals to indicate inductive effect operate the

Table 1. Spectral data of infrared frequencies (ν, cm^{-1}) and ^{13}C NMR chemical shifts (δ, ppm) of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones and substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepine-3(2H)-thiones.

S. No.	Substituent (X)	substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones					substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepine-3(2H)-thione				
		IR		^{13}C			IR		^{13}C		
		C=O	C-O-C	CO	N-Ar	ipso	C=S	C-O-C	CS	N-Ar	ipso
1	H	1660.27	1235.82	168.83	142.72	129.36	1161.35	1237.85	193.74	129.03	129.62
2	4-Br	1668.52	1238.24	169.34	143.92	122.38	1159.46	1238.33	194.06	130.92	126.71
3	3-Cl	1668.32	1237.70	169.82	143.76	134.32	1166.42	1238.21	193.10	130.11	135.62
4	4-Cl	1668.24	1235.00	169.43	143.07	133.28	1160.83	1238.89	193.85	129.68	134.11
5	4-$N(CH_3)_2$	1660.87	1221.81	166.8	140.36	154.12	1161.95	1235.10	192.16	129.32	158.72

6	4-F	1662.91	1235.23	167.11	142.31	161.78	1160.44	1238.12	193.16	130.62	159.14
7	4-I	1668.40	1236.71	168.72	141.00	112.36	1163.35	1237.97	193.82	130.71	118.26
8	3-OCH$_3$	1666.35	1222.17	166.14	140.28	160.84	1159.27	1234.35	192.12	129.16	159.23
9	4-OCH$_3$	1653.15	1232.12	166.21	140.32	158.12	1158.78	1234.32	192.28	129.27	159.44
10	3-CH$_3$	1668.21	1224.42	166.48	140.51	138.58	1155.28	1234.63	192.31	129.33	138.86
11	4-CH$_3$	1655.31	1225.05	166.43	140.62	136.22	1165.52	1235.01	192.3	129.68	137.62
12	3-NO$_2$	1680.25	1269.06	170.68	144.25	144.72	1161.73	1124.15	195.38	131.08	141.36
13	4-NO$_2$	1676.74	1269.01	170.74	144.36	144.86	1165.83	1241.94	195.26	131.01	141.41
14	3-CF$_3$	1670.74	1238.76	168.98	142.92	134.72	1160.35	1239.24	194.02	141.22	134.41

Table 2. Results of statistical analysis of IR and NMR spectral data of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-one with Hammett σ, σ+, σ_I, σ_R constants, F and R parameters

Frequency	Constants	r	I	ρ	s	n	Correlated derivatives
ν(C=O)cm^{-1}	σ	0.943	1663.92	15.88	4.23	13	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ$^+$	0.968	1662.21	7.387	5.68	12	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 3-OMe, 4-OMe, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.965	1659.70	20.45	5.71	11	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.956	1668.19	15.09	6.42	10	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F,3-OMe, 3-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.959	1659.88	18.41	6.23	11	H,4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.958	1669.44	12.98	6.32	10	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 3-Me, 3-NO$_2$, 4-NO$_2$,

ν(C-O-C)cm^{-1}	σ	0.963	1232.60	30.84	8.81	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.964	1237.04	13.85	11.78	11	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 4-OMe, 3-Me, 4-Me, 3-CF$_3$
	σ_I	0.978	1222.57	45.34	10.08	12	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-CF$_3$
	σ_R	0.956	1240.98	30.04	12.73	11	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-CF$_3$
	F	0.968	1222.65	41.76	11.27	13	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.963	1244.65	28.29	11.85	12	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-CF$_3$
δ(CO)ppm	σ	0.981	167.75	3.47	1.02	13	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.968	168.25	1.68	1.27	12	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.976	166.07	4.83	1.23	12	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.906	168.75	3.81	1.36	13	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.955	166.91	3.88	1.45	14	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.906	169.12	3.5	1.26	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
C-N	σ	0.978	141.69	3.18	1.03	13	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.971	142.15	1.66	1.17	12	H, 4-Br, 3-Cl, 4-Cl, 4-F, 4-I, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$

	σ_I	0.973	140.63	4.78	1.12	13	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.876	142.46	2.31	1.52	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.906	140.73	4.12	1.3	12	4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.889	142.93	3.11	1.26	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
δ(ipso)ppm	σ	0.876	142.01	-10.8	14.59	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.867	140.46	-6.15	14.6	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.866	140.43	-0.08	15.25	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.974	135.44	-39.2	10.23	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.845	137.07	-9.59	15.05	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.900	134.73	-23.4	12.91	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$

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

C=O ^{13}C NMR chemical shifts with all the substituents. The carbon NMR chemical shift values of N-Ar (δ, ppm) correlated with Hammett substituent constant and F and R parameters. The result of statistical analysis have shown good correlation with polar (σ (r = 0.978), σ+ (r = 0.971)), inductive (σ_I (r = 0.973)) Hammett constants and field effect (F (r = 0.906)), The remaining Hammett constant σ_R (r = 0.876) and Swain-Lupton parameter R(0.889) have shown poor correlation with all the substituents, it indicates, N-Ar bonding decreases the resonance effect. Then another carbon chemical shift of ipso-carbon involves correlated with Hammett resonance constant σ_R (r = 0.971) and resonance parameter R (r = 0.900) are shown satisfactory correlation, remaining Hammett constants (σ, σ^+ and σ_I) and one parameter (F) have been shown poor correlation, this result refer ipso-carbon decreases the polar, inductive and field effect of correlation coefficient, All the correlation have shown positive ρ value it is revel that the value of the reaction is more sensitive. The poor correlation observed in these correlations was attributed to the inability of effects of substituent and associated with the resonance-conjugative structure as shown in **Figure 3.**

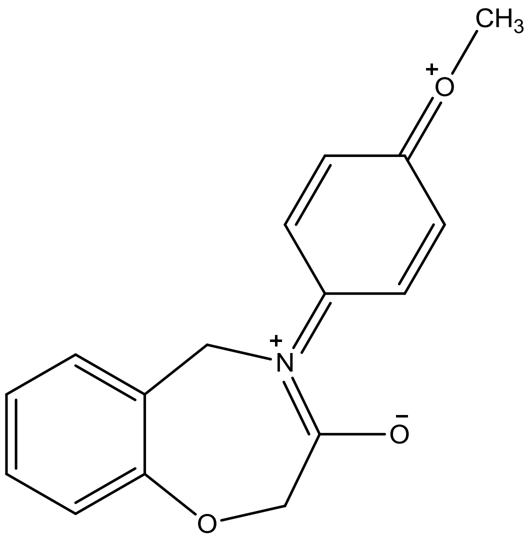


Figure 3. Resonance structure of substituted
4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones

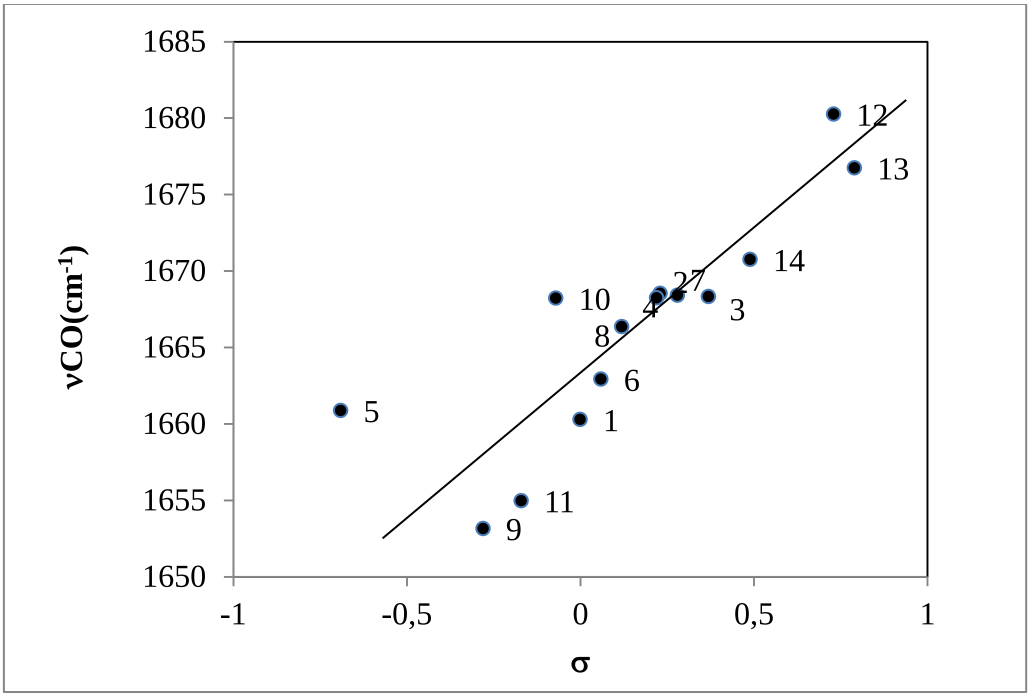


Figure 4. The plot of CO (ν, cm^{-1}) of substituted
4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones Vs σ.

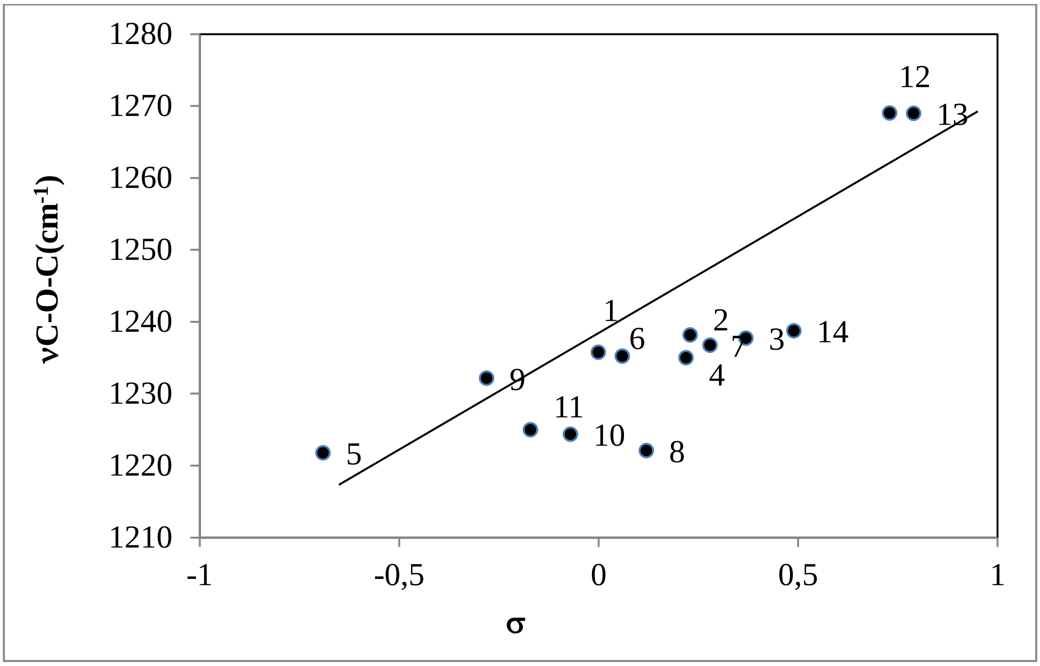


Figure 5. The plot of C-O-C (ν, cm^{-1}) of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones Vs σ.

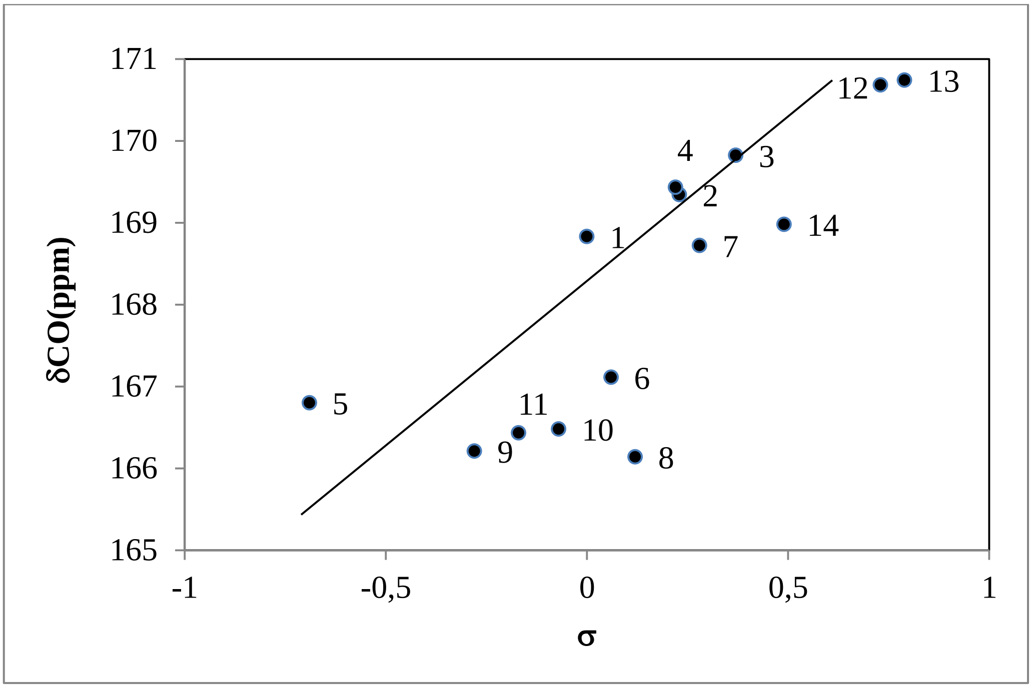


Figure 6. The plot of CO ^{13}C NMR spectral chemical shifts (δ, ppm) of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones.

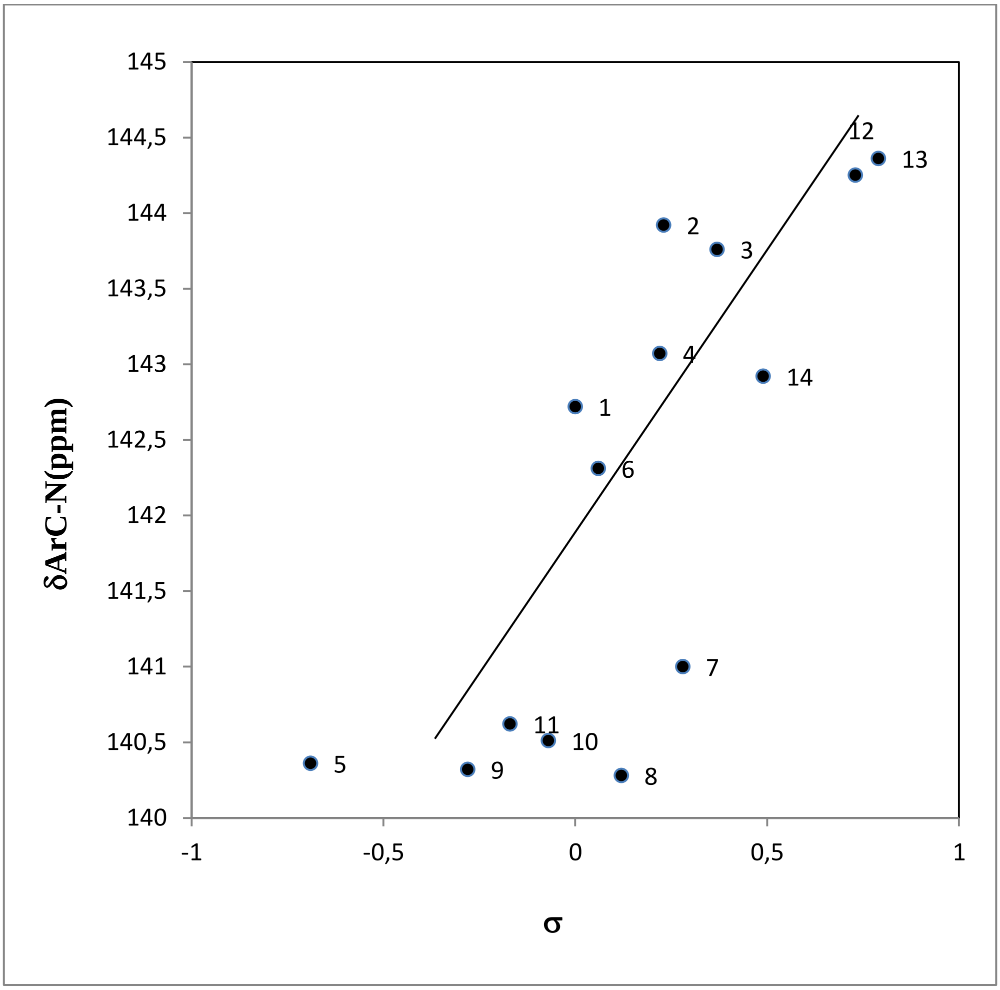


Figure 7. The plot of Aar-C-N ^{13}C NMR spectral chemical shifts (δ, ppm) of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones

Some of the single parameter correlation plots of infrared frequencies (ν, cm^{-1}) and ^{13}NMR spectral chemical shifts (δ, ppm) of substituted 4-phenyl-4,5-dihydrobenzo[f] [1,4]oxazepin-3(2H)-ones are shown in Figures 4-7.

3.2. Correlation analysis of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepine-3(2H)-thiones

From the Table 3, the infrared stretching frequency of (ν, cm^{-1}) C=S (1155.2-1166.4) correlated with Hammett constants (σ, σ^+, σ_I and σ_R), parameters F & R have shown poor correlation (r > 0.900) but multi-correlation analysis of inductive (σ_I) and resonance (σ_R) effect shown satisfactory correlation (r = 0.936), another one multi correlation of F(field effect) and R(resonance effect) parameters also shown more satisfactory correlation (r = 0.910). The sensitivity constant (ρ) shown positive values. This is revel that this reaction has more sensitivity and all the effect are operating normally.

Table 3. Results of statistical analysis of IR and NMR spectral data of substituted 4-phenyl- 4,5-dihydrobenzo[f][1,4]oxazepine-3(2H)-thiones with Hammett (σ, σ^+, σ_I, σ_R) constants and F & R parameters.

Freq.	Const.	r	I	ρ	s	n	Correlated derivative
$\nu C{=}S\ cm^{-1}$	σ	0.880	1161.87	2.308	3.04	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ^+	0.823	1162.37	1.232	3.07	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ_I	0.828	1160.23	3.483	3.06	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ_R	0.809	1162.36	3.314	3.04	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	F	0.805	1160.87	2.875	3.11	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	R	0.830	1162.09	1.986	3.12	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
$\nu C{-}O{-}C\ cm^{-1}$	σ	0.810	1233.23	-2.288	29.3	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ^+	0.810	1299.26	-1.137	30.5	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ_I	0.830	1242.39	-4.981	29.7	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	σ_R	0.830	1226.38	-2.732	30.5	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	F	0.831	1243.94	-3.989	29.9	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	R	0.828	1223.39	-2.085	30.3	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3

δCS ppm	σ	0.893	193.98	2.361	0.61	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.880	193.87	1.143	0.88	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.880	192.86	3.332	0.77	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.880	194.08	2.734	0.84	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.870	192.28	2.579	0.88	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.870	194.38	2.390	0.79	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
δ (N-Ar) ppm	σ	0.843	130.38	3.243	2.93	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.850	131.47	1.735	2.97	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.830	130.21	3.862	3.06	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_R	0.833	131.22	3.661	3.04	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	F	0.85	130.11	2.982	3.13	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	R	0.871	132.34	4.553	2.8	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
δ (ipso) ppm	σ	0.840	143.21	-1.533	12.5	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ^+	0.842	141.44	-8.221	12.6	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$
	σ_I	0.808	142.90	-4.346	13.8	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe$_2$, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO$_2$, 4-NO$_2$, 3-CF$_3$

	σ_R	0.870	136.08	-3.976	8.09	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	F	0.865	139.06	-4.718	13.8	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3
	R	0.841	135.05	-2.739	10.3	14	H, 4-Br, 3-Cl, 4-Cl, 4-NMe_2, 4-F, 4-I, 3-OMe, 4-OMe, 3-Me, 4-Me, 3-NO_2, 4-NO_2, 3-CF_3

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

The infrared stretching frequency of (ν, cm^{-1}) C-O-C (1124.1-1239.2) correlated with Hammett substituent constants and F & R parameters have shown less correlation coefficient value ($r > 0.900$). The multi correlation analysis [27] of C-O-C stretching frequency spectral value correlated with Hammett inductive (σ_I) and resonance (σ_R) constant (σ_I and σ_R, $r = 0.937$) and swain-Lupton constants [26] F and R shown good correlation effect (F and R, $r = 0.939$). The reaction constant ρ shown negative values. This is revels that operating reverse substituent effect and less sensitivity. The ^{13}C NMR chemical shift values of CS (δ, ppm 192.12-195.38) correlated with substituent constant and parameters, all the correlation have shown un satisfactorily gave less correlation coefficient value ($r > 0.900$). The multi correlation analysis of C-O-C stretching frequency spectral value correlated with Hammett inductive (σ_I) and resonance (σ_R) constant (σ_I and σ_R, $r = 0.990$) and swain-Lupton constants F and R shown good correlation effect (F and R, $r = 0.990$).

The chemical shift of N-Ar (δ, ppm, 129.03-141.22) correlated with Hammett (σ, σ^+, σ_I, σ_R) constants, F and R parameters were failing in correlations ($r > 0.900$). The failure in correlation was the inability of prediction of effects of substituents on the stretches and attributed with the resonance-conjugative structure as illustrated in **Fig. 8.**

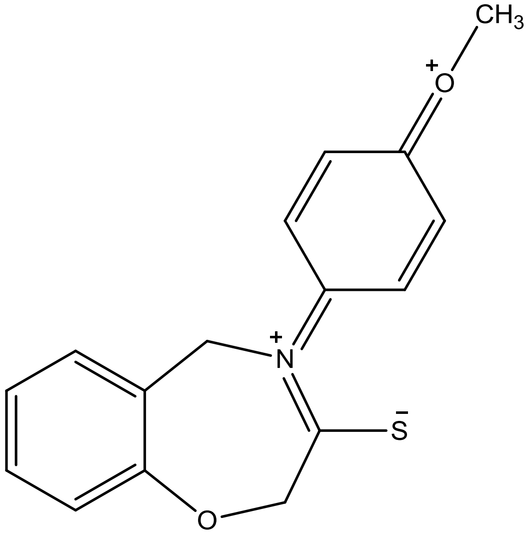


Figure 8. Resonance structure of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones

However, some of the correlation gave poor correlation coefficients for all spectral data of synthesized olanzapine ketones and thiones. While seeking these data in multi-regression [26] analysis above two systems of IR stretching frequencies and the carbon NMR chemical shifts have also produce satisfactory correlation shown equations (**3-21)** in the Table 4.

Table 4. The multi-regression analysis equations of 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones and 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones.

Multi-regression equation of 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones

$\upsilon C{=}O(cm^{-1}) = 1662.15(\pm2.55) + 17.18(\pm5.87)\,\sigma_I + 11.08(\pm3.21)\,\sigma_R$ ...(3)
(R = 0.956, n = 14, p > 95%)
$\upsilon C{=}O(cm^{-1}) = 1663.44(\pm 2.83) + 15.95(\pm5.99)\,F + 11.15(\pm4.01)\,R$ ...(4)
(R = 0.986, n = 14, p > 95%)
$\upsilon C\text{-}O\text{-}C(cm^{-1}) = 1227.19(\pm4.35) + 39.19(\pm10.04)\,\sigma_I + 20.87(\pm8.94)\,\sigma_R$ ...(5)
(R = 0.984, n = 14, p > 90%)
$\upsilon C\text{-}O\text{-}C(cm^{-1}) = 1230.35(\pm4.41) + 36.45(\pm9.31)\,F + 24.09(\pm6.74)\,R$ ...(6)
(R = 0.986, n = 14, p > 95%)
$\delta CO(ppm) = 167.34(\pm0.49) + 3.99(\pm1.14)\,\sigma_I + 2.88(\pm1.02)\,\sigma_R$ ...(7)
(R = 0.984, n = 14, p > 95%)
$\delta CO(ppm) = 167.91(\pm 0.56) + 3.19\,(\pm1.19)\,F + 3.13\,(\pm0.86)\,R$ ...(8)
(R = 0.982, n = 14, p > 95%)
$\delta N\text{-}Ar(ppm) = 140.92(\pm 0.56) + 4.39(\pm 1.29)\,\sigma_I + 1.29(\pm0.46)\,\sigma_R$ ...(9)
(R = 0.976, n = 14, p > 95%)
$\delta N\text{-}Ar(ppm) = 141.60(\pm 0.53) + 3.53(\pm 1.12)\,F + 2.71(\pm 0.80)\,R$ ...(10)
(R = 0.983, n = 14, p > 95%)
$\delta ipso(ppm) = 131.12(\pm5.16) + 12.33(\pm 3.90)\,\sigma_I - 42.12(\pm 10.60)\,\sigma_R$ …(11)
(R = 0.976, n = 14, p > 95%)
$\delta ipso(ppm) = 129.05(\pm 7.11) + 15.12(\pm 5.02)\,F - 25.10(\pm8.87)R$ ....(12)
(R = 0.958, n = 14, p > 95%)

Multi-regressionequation of 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones

$\upsilon C{=}S(cm^{-1}) = 1160.89(\pm1.57) + 2.69(\pm 0.61)\,\sigma_I + 2.68(\pm0.72)\,\sigma_R$ ...(13)
(R = 0.936, n = 14, p > 90%)
$\upsilon C{=}S(cm^{-1}) = 1160.96(\pm 1.7) + 2.49(\pm 0.71)\,F + 1.69\,(\pm 0.59)\,R$ ...(14)
(R = 0.910, n = 14, p > 90%)
$\upsilon C\text{-}O\text{-}C(cm^{-1}) = 1237.96(\pm15.46) - 35.08(\pm 12.65)\,\sigma_I - 19.05(\pm 6.75)\,\sigma_R$ ...(15)
(R = 0.937, n = 14, p > 90%)
$\upsilon C\text{-}O\text{-}C(cm^{-1}) = 1236.01(\pm16.71) - 34.78(\pm11.3)\,F - 21.20(\pm 7.12)R$ ...(16)
(R = 0.939, n = 14, p > 90%)

δCS(ppm) = 192.79(± 0.27) + 2.70 (± 0.62) σ_I + 2.07 (± 0.55) σ_R …(18)
(R = 0.990, n = 14, p > 95%)
δCS(ppm) = 193.06 (± 0.29) + 2.44(± 0.61) F + 2.11(± 0.44)R ...(17)
(R = 0.990, n = 14. P > 95%)
δN-Ar(ppm) = 130.21(± 1.56) + 2.98 ± 0.59) σ_I + 2.96(± 0.90) σ_R ...(18)
(R = 0.945. n = 14, p > 90%)
δN-Ar(ppm) = 131.14(±1.59) + 2.03 (±0.85)F + 4.32(± 1.43)R …(19)
(R = 0.952, n = 14, p > 95%)
δipso(ppm) = 133.38 (± 4.15) + 7.74(± 2.57) σ_I – 40.82(± 8.53) σ_R ...(20)
(R = 0.980, n = 14, p > 95%)
δipso(ppm) = 130.52(± 5.75) + 10. 84(±3.15) F – 27.77(±8.79) R …(21)
(R = 0.970, n = 14, p > 95%)

4. CONCLUSIONS

Each fourteen compounds of substituted 4-phenyl- 4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones and 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones have been prepared. Recorded the infrared and ^{13}C NMR spectra of these compounds. From the infrared spectra the C=O, C-O-C and C=S vibrations (ν, cm^{-1}) and ^{13}C NMR spectral chemical shifts(δ, ppm) of CO, CS, CN and ipso carbons of some oxazapine derivatives have been assigned and these area correlated with Hammett constant and F and R parameters using single and multi-regression analysis. From the results of statistical analysis the C=O, C-O-C stretches substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones gave satisfactory correlations. The ^{13}C NMR chemical shifts of CO groups of substituted 4-phenyl- 4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones gave satisfactory correlations. The C-N chemical shifts of substituted 4-phenyl-4,5-dihydrobenzo[f] [1,4]oxazepin-3(2H)-ones gave satisfactory correlations resonance components. The field and resonance effects of substituents gave satisfactory correlations for ipso carbon chemicals shifts of substituted 4-phenyl- 4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-ones. The C=S, C-O-C and C=S vibrations (ν, cm^{-1}) and ^{13}C NMR spectral chemical shifts(δ, ppm) of CO, CS, CN and ipso carbons of substituted 4-phenyl-4,5-dihydrobenzo[f][1,4]oxazepin-3(2H)-thiones gave poor correlations with hammett substituent constants and F and R parameters in single regression analysis. All spectral frequencies gave satisfactory correlation coefficients in multi-regression analysis with Swain-Lupton's parameters.

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