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FT-IR and NMR spectral LFER model analysis on some 3-(1-naphthyl)-1-substituted phenyl chalcones

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ABSTRACT

In this investigation, the authors predicted the effects of substituents on the functional groups of the titled chalcones using Linear Free Energy Relationship through Hammett equation with its constants and Swain-Lupton parameters. The LFER model statistical analysis was carried out using single and multi-linear regression analysis in MS Office 365 XL package. From the LFER analysis outcome, the influence of substituents on the spectroscopic functionality were discussed with their electronic effects such as, polar, inductive, resonance, field and conjugation. The titled compounds were prepared by solvent-free Aldol-Condensation method. The prepared compounds were characterised by their physical constants, micro analysis and spectroscopic data (FT-IR, NMR and Mass).

Keywords: 1-Naphthyl styryl ketone, Aldol condensation, IR and NMR Spectra, LFER Model

1. INTRODUCTION

LFER model analysis is the best tool for investigation of effect of substituents on the functional quantities such as kinetic (k) [1], equilibrium (K) [2], free energy(G) [3],

spectroscopic [4] and biological components IC or LD₅₀ [5]. These data are correlated using LFER model through Hammett equation using Hammett substituents constants and Swain-Lupton's [6] constants by single and multi-regression analysis. From the analysis results, scientists and chemists predicted the nature and probability-feasibility of reactions at the reaction center [1-5].

Various statistical equations are employed for the evaluation of LFER including Hammett equation such as Brønsted catalysis equation, Taft equation, Swain-Lupton equation, Grunwald-Winstein equation, Yukawa-Tsuno equation, Edwards equation, Marcus equation-quadratic free-energy relationship (QFER), Bell-Evans-Polanyi principle and Quantitative structure-activity relationships. Hammett equations applied for the *meta*- and *para*- substituted systems [8]. Taft equation employed for the prediction of LFER in *ortho*- substituted systems [9]. LFER analysis with infrared spectroscopic data of group frequencies (ν , cm⁻¹) of unsaturated carbonyl, alkenes, enone-enol systems gave the *s-cis* and *s-trans* conformations [10]. In nuclear magnetic resonance component analysis (Chemical shifts, δ , ppm) of alkene and unsaturated systems gave the probability-domination of effect of substituents on the *E* or *Z* geometric protons, vinyl and carbonyl carbons [11].

In recent years chemists and scientists employed the Hammett equation for prediction of effects of substituents on the spectral frequencies of various organic substrates such as unsaturated carbonyl compounds, alkenes, imines, pyrazolines, oxazoles, oxazanine-2-amines, sulfonamides, and Diels-Alder adducts [8-17]. Mihai et al., [18] studied the Brønsted type LFER study on the phospholipase C mechanism and they observed negative Brønsted coefficients for both nonenzymatic and enzymatic cleavage of aryl and non-hydrophobic alkyl inositol phosphates. Souza et al., [19] studied the proposed the reaction mechanism of reaction between γ -Methyl- β -alkynyl and an *ortho*-substituted aryl chloroformate ester through LFER analysis. Using Hammett and Taft equation, the various thermodynamic parameters were studied in many organic substrates [20].

The PP-LFERs is useful for characterization of equilibrium partitioning of organic chemicals in various environmental and technical partitioning systems and predict the respective partition coefficients [21]. This models also provides the idea of validating a new concept for the application of LFER in heterogeneous catalysis. Following this idea, the considered reactions center is the active site on the catalyst surface rather than that of the reacting molecule. The effect of solvent properties on ion pairing effects, direct application of Hammett's equation on polarographic data, entropic and enthalpic contributions to substituent effects and the quantum chemical interpretation of the reaction rate constant were studied through LFER Models on the reversible organic electrochemical reactions in aprotic solvents [22]. Bess and Sigman studied the asymmetric epoxidation reactions, asymmetric hydrogen bond catalyzed Diels-Alder reaction, asymmetric allylation of acetophenone, quadrupole moment to enantioselectivity in cation-O-mediated asymmetric polycyclization and Carton parameters to enantioselectivity in one two dimensional LFER models [23].

Quantum chemistry-kinetic analysis of experimental data on adsorption, hydrogenation, cracking, isomerization, and coking for various aromatic, hetero atom containing aromatics, and alkyl aromatics were analyzed through LFER models and reported by Neurock and Kelin [1]. SAR analysis of biological components with respect to the substituted bio-organic substrates through LFER models were reported by Thirunarayanan and Ranganathan [24].

Within the above view there is no report availed for the LFER model analysis of Hammett equation with spectroscopic data of 3-(1-naphthyl)-1-(substituted phenyl)-2-propen-1-ones in

the past. Hence, the authors taken effort to synthesized and recorded their IR and NMR spectra of above compounds for the study of LFER model.

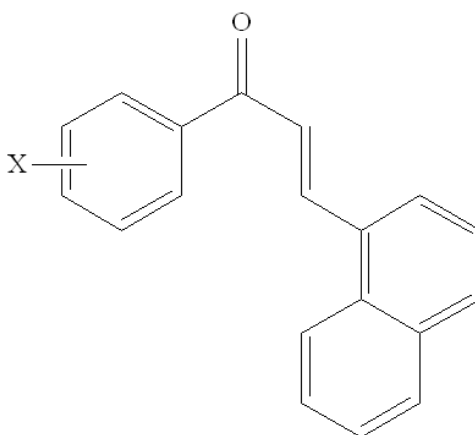
2. MATERIALS AND METHODS

2. 1. General

All chemicals used in this investigates were procured from Sigma-Aldrich chemical company. Avatar 300 type infrared spectrophotometer and Bruker 400 MHz NMR spectrometer were employed for recording IR and NMR spectra. MS Office 365 XL package used for LFER-Anova type statistical calculations.

2. 2. Preparation of 3-(1-naphthyl)-1-(substituted phenyl)-2-propen-1-ones

This series of chalcones were prepared by hydroxyapatite catalyzed solvent-free Aldol condensation method. Appropriate equimolar quantities of 1-naphthaldehyde (0.46 g, 2 mmol), acetophenones (0.240 g, 2 mmol) and hydroxyapatite (0.4 g) were taken in a 50 mL corning glass tube and tightly capped. The reaction mixture was subjected to microwave irradiation for 4-6 minutes in a microwave oven (LG Grill, Intellowave, Microwave Oven, 160-800W) and then cooled to room temperature. Added 10 ml of dichloromethane, the organic layer has been separated which on evaporation yields the solid product. The solid was recrystallized using ethanol to obtain pale yellow glittering solids. The structure of the compound was shown in Figure 1. The physico-chemical constants, analytical and Mass spectral fragments were employer for characterization of the compounds and the observations are acceptable with the data reported in literature [25-27].



X=H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-OCH₃, 3-NO₂, 4-NO₂

Figure 1. *E*-3-(1-naphthyl)-1-(substituted phenyl)-2-propen-1-ones

3. RESULTS AND DISCUSSION

3. 1. LFER analysis of IR data

The assigned infrared frequencies (ν , cm^{-1}) of the synthesized 3-(1-naphthyl)-1-(substituted phenyl) ketones were presented in Table 1. These data are correlated through

Hammett equation by single and multi-regression-LFER models. In this LFER model, the Hammett equation was employed as shown in equation (1).

$$v = v_0 + \rho\sigma \quad \dots (1)$$

where: v_0 vibrational frequencies of unsubstituted and v is the substituted system. The ρ is the reaction constant and it is depending on the reaction conditions. The σ is the substituent constants and these are independent of reactions.

Table 1. Infrared stretching frequencies (v , cm^{-1}) of 3-(1-naphthyl)-1-(substituted phenyl) ketones.

Entry	Substt.	CO <i>s-cis</i>	CO <i>s-trans</i>	CH _{ip}	CH _{op}	CH=CH _{op}	C=C _{op}
1	H	1661.55	1602.11	1207.88	781.53	1081.27	693.75
2	4-Br	1659.30	1600.00	1157.94	787.55	1091.55	696.56
3	3-Cl	1649.19	1608.25	1116.25	802.00	1019.95	630.21
4	4-Cl	1632.00	1600.95	1161.32	728.72	959.13	641.33
5	2-OH	1658.76	1599.28	1175.72	787.55	1004.44	670.34
6	3-OH	1669.41	1649.37	1172.48	798.85	1026.27	683.24
7	4-OH	1658.40	1606.23	1180.68	791.32	971.45	667.74
8	4-CH ₃	1688.28	1643.74	1217.26	772.11	1055.94	657.31
9	3-NO ₂	1688.68	1648.73	1169.82	772.24	1055.52	647.41
10	4-NO ₂	1686.35	1665.76	1217.04	773.03	1082.72	691.45

The synthesized 3-(1-naphthyl)-1-substituted phenyl chalcones exist as *s-cis* and *s-trans* conformers. These conformers are confirmed by the carbonyl group doublets obtained in the range of 1580-1686 cm^{-1} . They are shown in Figure 2 and the corresponding carbonyl frequencies (cm^{-1}) of the conformers are presented in Table - 1.

The assigned carbonyl stretches and deformation modes of 3-(1-naphthyl)-1-substituted phenyl chalcones have been correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. The results of statistical analyses are presented in Table - 2.

From the Table - 2, the correlation of $\nu\text{CO } s\text{-cis}$ (cm^{-1}) stretches gave poor correlations for Hammett σ constants, F and R parameters with positive ρ values. This is due to the incapability of prediction of effect of substituents on the carbonyl group by the substituents and associated with the resonance – conjugative structure as shown in Fig. 3.

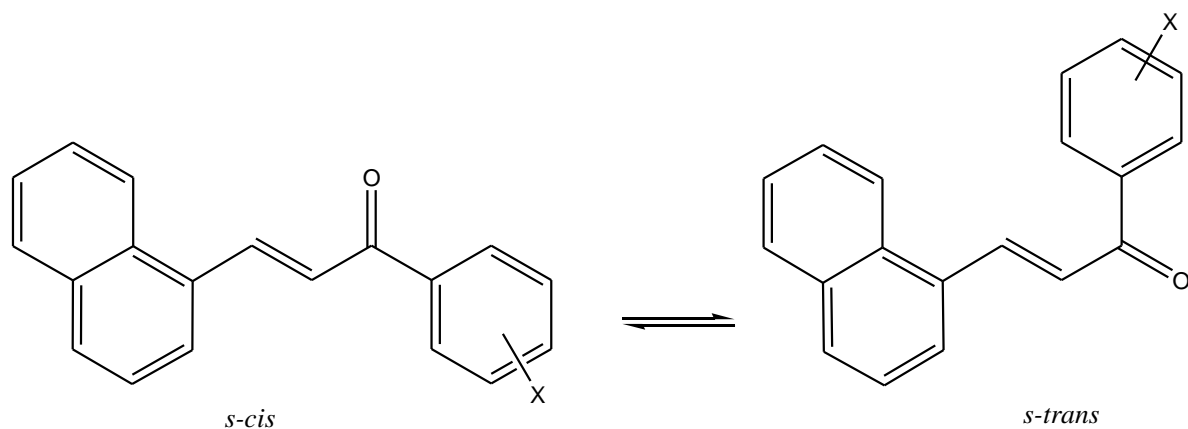


Figure 2. The *s-cis* and *s-trans* conformers of 3-(1-naphthyl)-1-substituted phenyl chalcones.

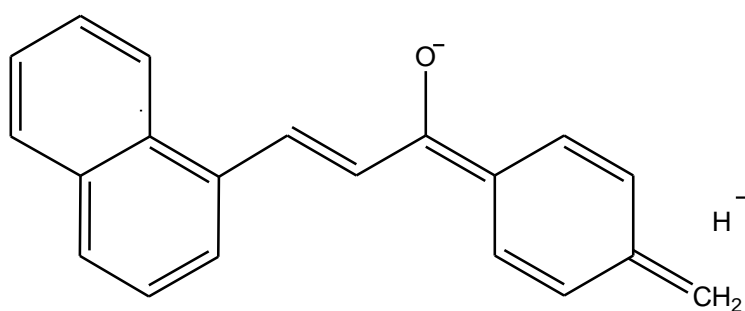


Figure 3. The resonance-conjugative structure of 3-(1-naphthyl)-1-(4-methylphenyl)-2-propen-1-one.

Table 2. LFER Model regression analysis of infrared $\nu(\text{cm}^{-1})$ CO_{s-cis} and $\text{CO}_{s-trans}$ 3-(1-naphthyl)-1-substituted phenyl chalcones with Hammett σ , σ^+ , σ_I , σ_R constants and F and R parameters.

Freq.	Constt.	r	I	ρ	s	n	Correlated derivatives
CO_{s-cis}	σ	0.729	1663.00	14.041	18.62	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.720	1665.13	6.436	19.08	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.791	1664.88	0.886	19.50	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_R	0.841	1671.28	4.524	17.23	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.807	1662.89	6.440	19.44	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.720	1668.18	9.432	19.00	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CO _{s-trans}	σ	0.900	1617.30	32.930	24.11	9	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 3-NO ₂ , 4-NO ₂
	σ^+	0.813	1622.33	11.026	26.80	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.823	1612.65	28.528	26.70	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.905	1631.52	52.327	23.98	9	4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.781	1609.96	35.051	26.41	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.801	1624.43	6.282	27.51	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
CH _{ip}	σ	0.811	1179.09	-9.318	32.48	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.801	1177.69	-6.288	32.47	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.784	1195.59	-52.340	29.87	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.827	1183.68	34.348	31.43	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.831	1195.20	-49.348	30.59	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.718	1181.63	12.604	32.18	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

CH_{op}	σ	0.823	781.41	-12.312	21.14	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.726	779.57	-9.464	21.22	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.716	784.44	-14.431	21.71	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.832	774.74	-2.079	20.82	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.711	783.41	-11.019	21.87	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.842	773.05	-20.781	19.98	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$CH=CH_{op}$	σ	0.808	1026.79	51.486	44.58	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.805	1034.42	42.311	41.75	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.802	1033.48	3.913	49.36	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.906	1055.59	118.02	38.32	9	H, 4-Br, 3-Cl, 2-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.700	1035.81	2.770	49.37	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.846	1056.66	49.960	43.59	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$C=C_{op}$	σ	0.710	668.93	-6.431	24.71	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_+	0.809	667.96	-3.634	24.75	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.719	673.97	-17.598	24.45	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_R	0.803	668.46	-3.015	24.84	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.714	673.56	-15.823	24.58	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.813	665.64	-7.222	24.63	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

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

The correlation of ν_{CO} *s-trans* (cm^{-1}) stretches were satisfactorily with Hammett σ and σ_R constants with positive ρ values excluding 3-OH and 4-Me substituents along with positive ρ values.

A satisfactory correlation was found for $\nu_{CH=CH_{op}}$ (cm^{-1}) deformation modes with Hammett σ_R substituent constants excluding 4-Cl and 3-OH substituents. The remaining Hammett substituent constants, F and R parameters were fail in correlations. All correlations gave positive ρ values.

This means that the normal substituent effects operated in all system. The correlation of $\nu_{C=C_{op}}$ (cm^{-1}) deformation modes with Hammett substituent constants, F and R parameters gave poor correlations along with negative ρ values. The negative ρ values implies that the reversal substituent effects operate in all ketones. The reasons for poor correlation was stated earlier and associated with the resonance conjugative structure as shown in Fig. 3.

In view of the inability of some of the σ constants to produce individually satisfactory correlations, it was thought that worthwhile to seek multiple correlations involving either σ_I and σ_R constants or Swain-Lupton's F and R parameters. The correlation equations for *s-cis*, *s-trans* and deformation modes were given in equations (2-13).

$$\nu_{CO(s-cis)}(\text{cm}^{-1}) = 1677.02(\pm 16.3057) - 14.166(\pm 7.217) \sigma_I + 39.596(\pm 6.273) \sigma_R \quad \text{---(2)}$$

$(R = 0.949, n = 11, P > 90\%)$

$$\nu_{CO(s-cis)}(\text{cm}^{-1}) = 1667.29(\pm 14.754) + 2.276(\pm 0.125) F + 9.174(\pm 1.543) R \quad \text{---(3)}$$

$(R = 0.922, n = 11, P > 90\%)$

$$\nu_{CO(s-trans)}(\text{cm}^{-1}) = 1627.61(\pm 18.431) + 9.968(\pm 3.811) \sigma_I + 48.806(\pm 6.371) \sigma_R \quad \text{---(4)}$$

$(R = 0.950, n = 11, P > 95\%)$

$$\nu_{CO(s-trans)}(\text{cm}^{-1}) = 1611.07(\pm 20.501) + 33.998(\pm 4.367) F + 2.337(\pm 0.687) R \quad \text{---(5)}$$

$(R = 0.929, n = 11, P > 90\%)$

$$\nu_{CH_{ip}}(\text{cm}^{-1}) = 1214.29(\pm 19.965) - 75.547(\pm 4.128) \sigma_I + 61.036(\pm 9.379) \sigma_R \quad \text{---(6)}$$

$(R = 0.961, n = 11, P > 95\%)$

$$\nu\text{CH}_{ip} (\text{cm}^{-1}) = 1204.46(\pm 22.766) - 58.133(\pm 4.849) F + 9.351(\pm 2.255) R \quad \text{---(7)}$$

($R = 0.944$, $n = 11$, $P > 90\%$)

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 776.76(\pm 16.088) - 4.907(\pm 3.329) \sigma_I - 25.061(\pm 3.206) \sigma_R \quad \text{---(8)}$$

($R = 0.932$, $n = 11$, $P > 90\%$)

$$\nu\text{CH}_{op} (\text{cm}^{-1}) = 773.808(\pm 15.460) - 1.906 (\pm 0.325) F - 20.064(\pm 1.621) R \quad \text{---(9)}$$

($R = 0.948$, $n = 11$, $P > 90\%$)

$$\nu\text{CH}=\text{CH}_{op} (\text{cm}^{-1}) = 1074.75(\pm 28.309) - 47.296(\pm 5.873) \sigma_I + 134.711(\pm 56.4261) \sigma_R \quad \text{---(10)}$$

($R = 0.967$, $n = 11$, $P > 95\%$)

$$\nu\text{CH}=\text{CH}_{op} (\text{cm}^{-1}) = 1061.21(\pm 33.514) - 26.871(\pm 7.138) F + 53.081(\pm 3.609) R \quad \text{---(11)}$$

($R = 0.948$, $n = 11$, $P > 90\%$)

$$\nu\text{C}=\text{C}_{op} (\text{cm}^{-1}) = 677.23(\pm 18.778) - 21.653(\pm 3.881) \sigma_I + 10.665(\pm 3.742) \sigma_R \quad \text{---(12)}$$

($R = 0.920$, $n = 11$, $P > 90\%$)

$$\nu\text{C}=\text{C}_{op} (\text{cm}^{-1}) = 670.84(\pm 18.984) - 13.242 (\pm 4.044) F - 5.685(\pm 2.044) R \quad \text{---(13)}$$

($R = 0.918$, $n = 11$, $P > 90\%$).

3. 2. LFER of NMR Spectra

3. 2. 1. ¹H NMR study

The prepared chalcones gave doublets for vinyl protons. These chemical shifts (δ , ppm) of doublets are tabulated in Table 3. In NMR spectral LFER model analysis, the Hammett equation was employed as in (14)

$$\delta = \delta_o + \rho\sigma \quad \dots (14)$$

where: δ_o chemical shifts of unsubstituted and δ is the substituted system. The ρ is the reaction constant and it is depends on the reaction conditions. The σ is the substituent constants and these are independent of reactions.

Table 3. The chemical shifts (δ , ppm) of vinyl proton, carbon and carbonyl carbons of 3-(1-naphthyl)-1-substituted phenyl chalcones.

Entry	X	H α	H β	CO	C α	C β
1	H	7.241	8.383	192.35	125.52	143.19
2	4-Br	7.508	8.681	189.18	124.03	142.34
3	3-Cl	7.598	8.689	189.01	124.09	142.31
4	4-Cl	7.487	8.210	189.91	124.11	140.76

5	2-OH	7.501	8.361	189.36	125.23	141.36
6	3-OH	7.528	8.656	188.10	123.59	141.27
7	4-OH	7.626	8.643	189.08	123.16	138.14
8	4-CH ₃	7.680	8.662	189.87	123.60	141.38
9	3-NO ₂	7.749	8.788	193.63	124.92	143.67
10	4-NO ₂	7.624	8.738	193.63	123.80	144.75

The assigned H_α and H_β chemical shifts (ppm) of 3-(1-naphthyl)-1-substituted phenyl chalcones were presented in Table 3. These chemical shifts were correlated with Hammett substituent constants, F and R parameters using single and multi-linear regression analysis. The results of statistical analyses were presented in Table 4. From Table 4, the Hammett σ , σ_R substituent constants and F parameters gave satisfactory correlation for H_α (ppm) chemical shifts excluding H, 4-OH, 4-CH₃ substituents. The Hammett σ^+ , σ_I substituent constants and R parameters gave poor correlation. All correlation gave positive ρ values. This shows that the normal substituent effects operate in all system. The reason for the poor correlation is due to the incapability of the substituents on the vinyl proton chemical shifts and is associated with the resonance-conjugated structure as shown in Fig. 3. The Hammett substituent constants, F and R parameters gave poor correlation for H_β (ppm) chemical shifts. The transmittance of the effect of substituents is significant for H_α (ppm) chemical shifts H_β (ppm) than chemical shifts.

Table 4. Results of statistical analysis of NMR chemical shifts (δ , ppm) of 3-(1-naphthyl)-1-substituted phenyl chalcones with Hammett substituent constants σ , σ^+ , σ_I , σ_R , F and R

Frequency	Constt.	r	I	ρ	s	n	Correlated derivatives
$\delta_{H\alpha}$ (ppm)	σ	0.903	7.536	0.112	0.12	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.703	7.553	0.039	0.28	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_I	0.804	7.465	0.258	0.25	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.901	7.569	0.086	0.19	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.905	7.440	0.319	0.11	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	R	0.811	7.562	0.026	0.24	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{\text{H}\beta}$ (ppm)	σ	0.839	8.550	0.195	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.826	8.580	0.086	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_{I}	0.781	8.486	0.276	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_{R}	0.734	8.631	0.285	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.831	8.466	0.332	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.810	8.595	0.041	10	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
δ_{CO} (ppm)	σ	0.906	189.85	3.568	1.52	7	H, 4-Cl, 2-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ^+	0.906	190.38	2.333	1.51	7	H, 4-Cl, 2-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_{I}	0.817	189.40	2.924	2.17	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_{R}	0.787	189.40	2.924	3.15	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.918	191.57	6.587	1.25	9	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.733	189.32	3.047	2.01	10	H, 4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta_{\text{C}\alpha}$ (ppm)	σ	0.913	124.16	0.271	0.80	7	4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂
	σ^+	0.931	124.20	0.401	0.77	7	4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂
	σ_{I}	0.701	124.30	0.300	0.81	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

	σ_R	0.813	124.27	0.422	0.80	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.812	124.33	0.361	0.81	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.832	124.39	0.589	0.77	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
$\delta C\beta$ (ppm)	σ	0.908	141.33	3.750	1.14	7	4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 3-NO ₂ , 4-NO ₂
	σ^+	0.910	141.89	2.590	1.05	7	4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 3-NO ₂ , 4-NO ₂
	σ_I	0.838	140.90	2.939	1.77	10	H, 4-Br, 3-Cl, 4-Cl, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	σ_R	0.907	142.88	5.515	1.26	9	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	F	0.833	140.90	2.789	1.81	10	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 3-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂
	R	0.906	142.76	2.660	1.47	9	H, 4-Br, 3-Cl, 4-Cl, 2-OH, 4-OH, 4-CH ₃ , 3-NO ₂ , 4-NO ₂

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

The application of Swain-Lupton's treatment to the relative chemical shifts of H _{α} and H _{β} of 3-(1-naphthyl)-1-substituted phenyl chalcones with F and R values is successful with resonance, inductive and fail with F & R parameter generates the multi regression equations (15-18).

$$\delta_{H\alpha} \text{ (ppm)} = 7.463(\pm 0.101) + 0.260(\pm 0.021) \sigma_I - 0.054(\pm 0.001) \sigma_R \quad \text{---(15)}$$

$(R = 0.944, n = 10, P > 90\%)$

$$\delta_{H\alpha} \text{ (ppm)} = 7.435 (\pm 0.091) + 0.324(\pm 0.021) F + 0.106(\pm 0.010) R \quad \text{---(16)}$$

$(R = 0.957, n = 10, P > 90\%)$

$$\delta_{H\beta} \text{ (ppm)} = 8.552(\pm 0.141) + 0.194(\pm 0.021) \sigma_I + 0.216(\pm 0.028) \sigma_R \quad \text{---(17)}$$

$(R = 0.943, n = 10, P > 90\%)$

$$\delta_{H\beta} \text{ (ppm)} = 8.547(\pm 0.146) + 0.318(\pm 0.031) F + 0.825(\pm 0.011) R \quad \text{---(18)}$$

$(R = 0.937, n = 10, P > 90\%)$

3. 2. 2. ¹³C NMR Spectral LFER

The assigned carbonyl and vinyl carbon C_α and C_β chemical shifts (ppm) in 3-(1-naphthyl)-1-substitutedphenyl chalcones were correlated with Hammett sigma constants and F and R parameters. The results of statistical analyses are presented in **Table 4**. From the **Table 4**, Hammett σ, σ⁺ substituent constants and F parameters were satisfactorily correlated for carbonyl carbon chemical shifts (ppm) excluding 4-Br, 3-Cl, 2-OH and 4-OH substituents. The Hammett σ_I, σ_R substituent constants and R parameters were fail in correlation. All correlation gave positive ρ values. The reason for poor correlation is stated as in earlier section and associated with the resonance – conjugative structure as shown in **Fig. 3**.

From the results of statistical analysis presented in **Table 4**, The C_α chemical shifts (ppm) of 3-(1-naphthyl)-1-substitutedphenyl chalcones correlated satisfactorily with Hammett σ, σ⁺, constants excluding H, 2-OH and 4-NO₂ substituents. The Hammett σ_I, σ_R constants F and R parameters were fail in correlation. All correlations gave positive ρ values. This shows that there is a normal substituent effects operates in all systems. The reason for poor correlation is stated earlier and associated with the resonance – conjugative structure as shown in **Fig. 3**.

The C_β chemical shifts (ppm) of substituted styryl 3-(1-naphthyl)-1-substitutedphenyl chalcones were satisfactorily correlated with Hammett σ, σ⁺, σ_R and R constant excluding H, 2-OH, 3-OH, 4-OH and 4-CH₃ substituents. The remaining Hammett σ_I constants and F parameters were fail in correlation. All correlations gave positive ρ values. This shows that there is a normal substituent effects operates in all systems. The failure in correlation was due to the reasons stated earlier and is associated with the resonance-conjugative structure as shown in **Fig. 3**. The degree of transmission of substituent effects on C_β is more sensitive than that of C_α carbons.

Some of the single parameter correlation were fail for the Hammett substituent constants, F and R parameters. They shows satisfactory correlations in multi-regression analysis with Swain Lupton's parameters.

The generated multi- regression equations are given in (19-24).

$$\delta_{CO} \text{ (ppm)} = 191.37(\pm 0.963) + 0.485(\pm 0.011) \sigma_I + 6.415(\pm 0.192) \sigma_R \quad \text{---(19)}$$

(R = 0.981, n = 10, P > 95%)

$$\delta_{CO} \text{ (ppm)} = 190.94(\pm 1.027) + 1.514(\pm 0.218) F + 3.376(\pm 1.117) R \quad \text{---(20)}$$

(R = 0.978, n = 10, P > 95%)

$$\delta_{C\alpha} \text{ (ppm)} = 124.49(\pm 0.617) + 0.532(\pm 0.127) \sigma_I + 0.609(\pm 0.123) \sigma_R \quad \text{---(21)}$$

(R = 0.920, n = 10, P > 90%)

$$\delta_{C\alpha} \text{ (ppm)} = 124.65(\pm 0.586) + 0.670(\pm 0.124) F + 0.663(\pm 0.013) R \quad \text{---(22)}$$

(R = 0.938, n = 10, P > 90%)

$$\delta_{C\beta} \text{ (ppm)} = 142.49(\pm 0.951) + 0.972(\pm 0.197) \sigma_I + 5.175(\pm 0.190) \sigma_R \quad \text{---(23)}$$

(R = 0.976, n = 10, P > 95%)

$$\delta_{C\beta} \text{ (ppm)} = 142.11(\pm 1.109) + 1.648(\pm 0.236) F + 2.469(\pm 0.1014) R \quad \text{---(24)}$$

(R = 0.967, n = 10, P > 95%)

4. CONCLUSIONS

The authors prepared some *E*-3-(1-naphthyl)-1-substituted phenyl chalcones by solvent-free aldol-condensation method. The assigned infrared and nmr spectral frequencies were correlated through LFER model for investigating the effects of substituents. From the LFER model regression analysis results, the correlation of ν_{CO} *s-trans* (cm^{-1}) stretches were satisfactorily with Hammett σ and σ_{R} constants with positive ρ values excluding 3-OH and 4-Me substituents.

A satisfactory correlation was found for $\nu_{\text{CH}=\text{CH}_{op}}$ (cm^{-1}) deformation modes with Hammett σ_{R} substituent constants excluding 4-Cl and 3-OH substituents. The Hammett σ , σ_{R} substituent constants and F parameters gave satisfactory correlation for H_{α} (ppm) chemical shifts excluding H, 4-OH, 4-CH₃ substituents. The Hammett σ , σ^{+} substituent constants and F parameters were satisfactorily correlated for carbonyl carbon chemical shifts (ppm) excluding 4-Br, 3-Cl, 2-OH and 4-OH substituents. The C_{α} chemical shifts correlated satisfactorily with Hammett σ , σ^{+} , constants excluding H, 2-OH and 4-NO₂ substituents.

The C_{β} chemical shifts (ppm) were satisfactorily correlated with Hammett σ , σ^{+} , σ_{R} and R constant excluding H, 2-OH, 3-OH, 4-OH and 4-CH₃ substituents.

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