The Correlation Analysis of Substituents Effect on ^{13}C NMR Chemical Shifts of E-2-(-4'-X-benzylidene)-1-indanones, -tetralones, –benzosuberones and Chalcones

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Abstract

The ^{13}C Substituent Chemical Shifts (**SCS**) effect on $(C_\alpha)C_2$, C_{9a}, $(C_\beta)C_{10}$ and $C_{1'}$ atoms for **E-2-(-4'-X-benzylidene)-1-indanones, -tetralones, –benzosuberones and Chalcones** (**X= H, NMe$_2$, OMe, Me, F, Cl, Br, CN, NO$_2$**) in **CDCl$_3$** solvent. The effect was studied using two different types of substituent parameter: namely mono substituent parameter **MSP (σ^{13} model, Hammett's and the Brown-Okamoto models),** and dual substituent parameters **DSP (modified Swain-Lupton, Reynolds, Taft and modified Godfrey models).** Both **MSP** and **DSP** models reflected that the resonance effect contributes more on the chemical shift of $(C_\alpha)C_2$, while inductive effects primarily affect the chemical shift of $(C_\beta)C_{10}$ of the enone moiety of all the four series. The latter effect, however, is far not as pronounced as that of the former one. It is found that **DSP** model (ρ_F and ρ_R values) of ^{13}C **SCS** effect on C_2 can serve as a measure to study the conformation (or the planarity) of the investigated enones in the four series. Finally, **MSP** and **DSP** models performance are performed.

1. Introduction

The chemical shifts in ^{13}C **NMR** spectra are very convenient to study the transmission of electronic effects of substituents in organic molecules, being exceptionally sensitive to the distribution of electronic density at particular carbon atoms. The most frequently used analysis of ^{13}Csubstituent chemical shifts (**SCS**) is based on the principles of linear free energy relationships (**LFER**) comprising the **MSP** (mono substituent parameter) (equation **1**) or **DSP** (dual substituent parameter) (equation **2**) in the forms:

$$SCS = \rho\sigma \qquad\qquad (1)$$
$$SCS = \rho_I\sigma_I + \rho_R\sigma_R \qquad (2)$$

where **SCS** are the substituent chemical shifts, ρ is the proportionality constant reflecting the sensitivity of the ^{13}C **NMR** chemical shifts to substituent effects , σ is the corresponding substituent constant. ρ_I and ρ_R are weighing factors for the field/inductive and resonance effect respectively.

It is well demonstrated in the literature that **NMR** chemical shifts are sensitive probes of electron-density distributions and are useful for the studying the transmission of electronic effects in organic molecules. Several workers have found very good linear free energy relationships between Hammett σ constants [1] or commonly between Brown and Okamoto's σ^+ constants [1] and the ^{13}C **NMR** chemical shifts of the β-carbon of chalcones and chalcone derivatives [2-4]. Reynolds et al. [5] demonstrated that, ^{13}C **NMR** chemical shifts can be used to monitor changes in ground state electron distributions in styrene derivatives and that **DSP** correlations with field and resonance

parameters can be used to deduce mechanisms of transmission of electronic effects. Earlier Perjesi et al. performed such ^{13}C **NMR** study on E-2-(X-benzylidene)-1-cyclohexanones [6] and E-2-(X-benzylidene)-1-indanones [7] to interpret to what extent the spectroscopic data reflect the stereostruture and the electronic distribution of the compounds. As a continuation of these previous works of Perjesi et al. reported on the ^{13}C NMR investigations of transmission of substituent effects in the title E-2-(X-benzylidene)-1-indanones, -tetralones and –benzosuberones applying mono substituent parameter (MSP) and dual substituent parameter(DSP) analyses, comparative investigation on the transmission of the electronic effects by substituents in E-2-(X-benzylidene)-1-indanones and chalcones is also reported. The aim of this study, to investigate the performance of different types of models **MSP** and **DSP**, and to compare their performance in describing the transmission of substituent effect.

2. Procedure

The ^{13}C **NMR** substituent chemical shifts of **C_2, C_{9a}, C_{10}** and **$C_{1'}$**of E-2-(X-benzylidene)-1-indanones, -tetralones and –benzosuberones[4, 5] with **"basis set"** substituents were modeled by different types of substituent parameter, **DSP** and **MSP** models. The single and multiple regressions were performed on **Pentium (IV) PC** with statistical program by using stepwise regression procedure by computer program, called **Minitab version 11.11(MTB).** The

statistical parameter **f-Taft (SD/RMS)** was used to judge the quality for these models, (where **SD** is standard deviation of estimation, and **RMS** is root mean squares of the analyzed data). The smaller the **f** value the better the fit. With values of **0.0-0.1** representing excellent correlations, while **f** values of **0.1-0.3** moderately good ones, and **f** values are greater than **0.3** representing only crude trends [**8**].
Modification of Godfrey model;

$$\delta P = \rho[\sigma ST - \lambda(\sigma ST - \sigma I)] \quad ----------- (a) \; [Godfrey\ model][9]$$
$$But, \quad \sigma R, ST = \sigma ST - \sigma I \quad ---------- (b)$$
$$\delta P = \rho[\sigma ST - \lambda \sigma R, ST] \quad ------------ (c)$$
$$\delta P = \rho[\sigma I - \sigma R, ST - \lambda \sigma R, ST] \quad --------- (d)$$
$$\delta P = \rho[\sigma I + (1 - \lambda)\sigma R, ST] \quad --------- (e)$$
$$\delta P = \rho \sigma I + \rho(1 - \lambda)\sigma R, ST \quad --------- (f) \; [Modified\ Godfrey\ model]$$

σST is the $^{13}C_\beta$ **SCS** in the ring-substituted styrenes [5] expressed in units of 5 ppm.
We can use modified Godfrey model as a DSP model.

3. Results and Discussion

The ^{13}C substituent chemical shift **SCS** effects on the C_2, C_{9a}, C_{10} and $C_{1'}$ of E-2-(X-benzylidene)-1-indanones, -tetralones and –benzosuberones, **series [a, b, c and d]** respectively **[7, 10] Scheme 1,** are listed in **[Table 1]**. The **SCS** effect represents the difference in the chemical shift between the substituted and unsubstituted derivatives. The data were modeled by two different types of substituent parameter: namely mono substituent parameter (**MSP**) (σ^{13} **model [11] Hammett's and the Brown-Okamoto models [1]),** and dual substituent parameter **DSP (modified Swain-Lupton[1],**

Reynolds' [5], Taft [12] and modified Godfrey [9] models).

The statistical **f-Taft (SD/RMS)** was used to judge the quality of correlation, which is more sensitive than linear correlation coefficient (**r**), or multiple regression coefficient (**R**), and **F-Snedecor** in comparisons of narrowly different model **[13]**, "normal" and "reverse" effects to refer to the situations when electron with-drawing substituents induce downfield and upfield chemical shifts, respectively (and vice-versa for donors) **[14]**.

a (n=1);   b (n=2);   c (n=3)   d

X= H, NMe$_2$, OMe, Me, F, Cl, Br, CN, NO$_2$

Scheme 1.

Table 1. ^{13}C SCS effects on C_2, C_{9a}, C_{10} and $C_{1'}$ of the series [a, b, c and d]: E-2-(4'-X-benzylidene)-1-indanones, -tetralones, –benzosuberones and chalcones respectively;

Substituent	[a]				[b]			
	C_2	C_{9a}	C_{10}	$C_{1'}$	C_2	C_{9a}	C_{10}	$C_{1'}$
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NMe$_2$	-5.0	0.8	1.0	-12.2	-4.4	0.6	1.2	-12.3
OMe	-2.4	0.3	-0.2	-7.2	-1.9	0.2	0.0	-7.5
Me	-1.0	0.2	0.0	-2.7	-0.7	0.1	0.2	-2.9
F	-0.5	0.0	-1.3	-3.6	-0.2	0.0	-1.1	-3.9
Cl	0.4	-0.1	-1.5	-1.5	0.5	-0.1	-1.4	-1.6
Br	0.6	-0.1	-1.5	-1.1	0.6	-0.1	-11.4	-1.1
CN	3.1	-0.4	-2.6	4.4	2.6	-0.4	-2.6	4.7
NO$_2$	3.8	-0.4	-3.1	6.4	3.1	-0.4	-3.0	6.7

Substituent			[c]				[d]	
	C_2	C_{9a}	C_{10}	$C_{1'}$	C_2	C_{9a}	C_{10}	$C_{1'}$
H	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
NMe$_2$	-4.7	0.8	0.5	-12.5	-5.2	0.8	1.0	-12.3
OMe	-2.1	0.3	-0.3	-7.5	-2.4	0.3	-0.2	-7.3
Me	-0.8	0.1	0.0	-2.9	-1.0	0.1	0.1	-2.8
F	-0.3	-0.1	-1.3	-3.9	-0.3	-0.1	-1.3	-3.8
Cl	0.6	-0.2	-1.5	-1.5	0.3	-0.2	-1.6	-1.5
Br	0.7	-0.2	-1.4	-1.1	0.4	-0.2	-1.5	-1.1
CN	2.8	-0.7	-2.5	4.7	2.9	-0.7	-2.8	4.2
NO$_2$	3.3	-0.8	-2.9	6.7	3.6	-0.7	-3.4	6.1

The correlation analysis of ^{13}C SCS effects on C_2, C_{9a}, C_{10} and $C_{1'}$of Series **[a, b, c and d]: E-2-(X-benzylidene)-1-indanones, -tetralones, –benzosuberones and chalcones** respectively when σ^{13} **model is used [Table 2]**, C_2, gave an excellent correlation in series **[b, c and d]** while series **[a]** gave a moderately good, with normal ρ values [3.202, 2.724, 2.927 and 3.178] for series **[a, b, c and d]** respectively. The lower transmission efficiency in the E-2-(X-benzylidene)-1-tetralones, and –benzosuberones is evidently caused by the preference of the non-planar enone structure and the non-planar arrangement of the aryl ring and the enone moiety of the compounds as it was determined by X-ray crystallography **[15, 16]**. On the contrary, the open-chain s-cis chalcones **[17]** and E-2-(X-benzylidene)-1-indanones, in particular **[18]**, adopt a rather planar structure. $C_{1'}$gave a moderately good correlation with all series, with normal ρ values [6.657, 6.839, 6.904 and 6.09] for series **[a, b, c and d]** respectively. C_{10}, is less sensitive to the substituent effects, with negative (reverse substituent effect) ρ values [-1.476, -1.541, -1.248 and -1.578] for series **[a, b, c and d]** respectively, which show crude trends correlation with all series. The ρ values obtained do not show clear relationship with planarity of the compounds of the four series. C_{9a}, shows the same behavior as C_{10}, but with a moderately good correlation with all series.

Table 2. Correlation analysis of ^{13}C SCS effects on C_2, C_{9a}, C_{10} and $C_{1'}$for the series [a, b, c and d]: E-2-(X-benzylidene)-1-indanones, -tetralones, –benzosuberones and chalcones respectively on using σ^{13} model.

a:

C atom	ρ	S.D	r	F	f-Taft
C_2	3.202±0.14	0.3357	0.9930	493.97	0.134
C_{9a}	-0.448±0.02	0.0414	0.9945	635.96	0.118
C_{10}	-1.476±0.25	0.5818	0.9127	34.94	0.359
$C_{1'}$	6.657±0.51	1.1960	0.9798	168.30	0.213

n (number of substituents) = 9; r = linear correlation coefficient; F = F-Snedecor.

b:

C atom	ρ	S.D	r	F	f-Taft
C_2	2.724±0.07	0.1577	0.9980	1619.21	0.074
C_{9a}	-0.370±0.01	0.0305	0.9955	796.86	0.106
C_{10}	-1.541±0.24	0.5591	0.9247	41.25	0.355
$C_{1'}$	6.839±0.57	1.327	0.9767	144.18	0.229

n = 9; r = linear correlation coefficient; F = F-Snedecor.

c:

C atom	ρ	S.D	r	F	f-Taft
C_2	2.927 ± 0.09	0.1991	0.9970	1172.73	0.080
C_{9a}	-0.584 ± 0.03	0.0760	0.9894	320.36	0.163
C_{10}	-1.248 ± 0.26	0.6120	0.8735	22.59	0.402
$C_{1'}$	6.904 ± 0.55	1.2930	0.9783	154.87	0.222

n = 9; r = linear correlation coefficient; F = F-Snedecor.

d:

C atom	ρ	S.D	r	F	f-Taft
C_2	3.178 ± 0.09	0.2187	0.9970	1146.37	0.088
C_{9a}	-0.563 ± 0.03	0.0764	0.9910	379.31	0.150
C_{10}	-1.578 ± 0.28	0.6519	0.9055	31.81	0.377
$C_{1'}$	6.609 ± 0.51	1.1920	0.9798	166.99	0.212

n = 9 r = linear correlation coefficient; F = F-Snedecor.

On using **Hammett's [σ] and the Brown-Okamoto [σ^+] models [Table 3]**, the results of analysis of the C_2, C_{9a}, C_{10} and $C_{1'}$ of ^{13}C SCS effect with both σ and σ^+ constants resulted in a moderately good correlations in all series, except C_{10} with σ^+ representing only crude trends. The C_2 and $C_{1'}$ with the higher ρ values, indicating a significant resonance interaction between the substituents and the C_2 and the $C_{1'}$ carbon atoms. Similar conclusion could be drawn from the MSP analysis of the IR carbonyl stretching wave numbers of series **[a, b and c] [4]**. It is worth mentioning that the respective regression coefficient of ρ values obtained for the MSP analysis of the IR carbonyl stretching wave number (e.g. for the σ values ρ =12.00, 7.95, 6.41 and 9.41 **[2]** in the series **[a, b, c and d]**, respectively) follows a similar decreasing tendency as that obtained for the ^{13}C SCS of C_2 (for the σ values: ρ = 5.422, 4.595, 4.952 and 5.356 for series **[a, b, c and d]**, respectively) in the four series. Accordingly, sensitivity of the IR carbonyl stretching wave numbers and that of the ^{13}C SCS effect of C_2 to the polar effects of substituents (expressed by the Hammett σ constants) seem to be mainly the inductive effect due to the planarity of chalcones and their cyclic analogues.

The chemical shift of the C_{10} atom is less sensitive to the substituent effects (for the σ values: ρ = -2.629, -2.736, -2.258 and -2.824 for the series **[a, b, c and d]**, respectively) than that of C_2 and its correlation with the σ and σ^+ parameters gives a linear relationship of opposite (negative) slope. Similar conclusion has been drawn on earlier ^{13}C **NMR** investigation of chalcones as well **[4]**. In addition, this study demonstrated that the MSP regression coefficients ρ obtained for the ^{13}C **SCS** effect values of C_{10} do not show clear relationship with planarity of the compounds of the four series. The C_{9a} atoms, shows the same behavior as C_{10} atoms.

A comparison between **Hammett's model** and σ^{13} **model**, C_2 and $C_{1'}$ for all series are the best in σ^{13} **model**, while for C_{10}, **Hammett's model** is the best one. For C_{9a}, series **[a]**, both models are the same quality, while for series **[b]**, σ^{13} **model,** is the best, but for both series **[c and d]**, **Hammett's model** is the best.

Table 3. Correlation analysis of ^{13}C SCS effects on C_2, C_{9a}, C_{10} and $C_{1'}$ for the series [a, b, c and d] on using Hammett's (σ) and the Brown-Okamoto (σ^+) models.

a:

C atom	Parameter	ρ	S.D	R	F	f-Taft
C_2	σ	5.422±0.26	0.3515	0.9925	450.01	0.140
	σ^+	3.469±0.24	0.5019	0.9844	217.13	0.200
C_{9a}	σ	-0.753±0.05	0.0630	0.9874	270.14	0.179
	σ^+	-0.789±0.02	0.0422	0.9945	610.05	0.120
C_{10}	σ	-2.629±0.29	0.4001	0.9597	81.68	0.247
	σ^+	-1.580±0.30	0.6376	0.8944	27.91	0.394
$C_{1'}$	σ	11.079±1.18	1.6280	0.9623	87.61	0.289
	σ^+	7.223±0.65	1.3890	0.9726	122.95	0.247

b:

C atom	Parameter	ρ	S.D	R	F	f-Taft
C_2	σ	4.595±0.20	0.2765	0.9935	522.38	0.130
	σ^+	2.959±0.14	0.3080	0.9920	419.63	0.145
C_{9a}	σ	-0.626±0.03	0.0348	0.9945	611.82	0.121
	σ^+	-0.402±0.02	0.0474	0.9894	326.12	0.164
C_{10}	σ	-2.736±0.26	0.3624	0.9690	107.82	0.230
	σ^+	-1.652±0.29	0.6182	0.9072	32.45	0.392
$C_{1'}$	σ	11.407±1.24	1.7000	0.9612	85.10	0.294
	σ^+	7.412±0.72	1.5370	0.9685	105.66	0.265

c:

C atom	Parameter	ρ	S.D	R	F	f-Taft
C_2	σ	4.952±0.21	0.2934	0.9935	536.61	0.129
	σ^+	3.180±0.16	0.3382	0.9915	401.89	0.148
C_{9a}	σ	-0.997±0.03	0.0392	0.9970	1224.92	0.084
	σ^+	-0.630±0.05	0.1083	0.9783	154.14	0.232
C_{10}	σ	-2.258±0.33	0.4534	0.9327	46.88	0.298
	σ^+	-1.329±0.31	0.6604	0.8515	18.41	0.433
$C_{1'}$	σ	11.511±1.23	1.6900	0.9623	87.77	0.290
	σ^+	7.486±0.70	1.5000	0.9706	113.18	0.257

d:

C atom	Parameter	ρ	S.D	R	F	f-Taft
C_2	σ	5.356±0.27	0.3656	0.9915	405.81	0.147
	σ^+	3.448±0.19	0.4030	0.9894	332.82	0.162
C_{9a}	σ	-0.959±0.03	0.0462	0.9955	814.19	0.103
	σ^+	-0.610±0.04	0.0946	0.9818	189.37	0.211
C_{10}	σ	-2.824±0.33	0.4497	0.9560	74.57	0.260
	σ^+	-1.684±0.34	0.7167	0.8843	25.11	0.414
$C_{1'}$	σ	10.987±1.19	1.6410	0.9612	84.76	0.292
	σ^+	7.178±0.64	1.3570	0.9737	127.13	0.241

n = 9; r = linear correlation coefficient; F = F-Snedecor.

In order to get a further estimation of the relative importance of the substituent's inductive (field) and resonance effects, DSP analysis of the ^{13}C **SCS** effect were performed employing Eq. **(2)**. The results of the DSP correlation obtained for the selected ^{13}C **NMR** chemical shifts of the series [a, b, c and d] are listed in [**Tables 4-7**], using **modified Swain-Lupton, Reynolds, Taft** and **modified Godfrey models** respectively.

On using a modified Swain-Lupton model **[Table 4]**, C_2 gave an excellent correlations for all series, with a normal reaction constants for both a field **(f)** and a resonance **(r)**, with a blending constants λ in the range (1.402-1.464). The C_{9a} atoms, gave an excellent correlations for series **[b and c]**, while series **[a and d]** gave a moderately good correlations, with a reverse reaction constants for both a field and a resonance, with a blending constants λ in the range (1.062-1.358). The C_{10}, gave an excellent correlations for series **[a, b and d]**, while series **[c]** gave a moderately good correlation, with a reverse reaction constants for both a field and a resonance, with a blending constants λ in the range (0.353-0.494). The $C_{1'}$, gave a moderately good correlations for all series, with normal reaction constants for both a field and a resonance, with a blending constants λ in the range (2.497-2.684).

Table 4. DSP Correlation analysis of ^{13}C SCS effects of the C_2, C_{9a}, C_{10} and $C_{1'}$ for the series [a, b, c and d] on using modified Swain-Lupton model.

a:

C atom	f	r	λ	S.D	R	F	f-Taft
C_2	4.277±0.35	6.010±0.22	1.405	0.2108	0.9975	632.40	0.084
C_{9a}	-0.609±0.09	-0.827±0.06	1.358	0.0553	0.9915	177.10	0.157
C_{10}	-4.145±0.18	-1.851±0.12	0.447	0.1097	0.9975	587.29	0.068
$C_{1'}$	5.450±1.36	13.969±0.87	2.563	0.8260	0.9920	180.72	0.147

b:

C atom	f	r	λ	S.D	R	F	f-Taft
C_2	3.584±0.18	5.114±0.11	1.427	0.1073	0.9990	1754.13	0.051
C_{9a}	-0.520±0.04	-0.680±0.02	1.309	0.0236	0.9980	670.80	0.082
C_{10}	-4.111±0.16	-2.031±0.10	0.494	0.0975	0.9980	790.87	0.062
$C_{1'}$	5.735±1.59	14.319±1.01	2.497	0.9630	0.9894	140.58	0.166

c:

C atom	f	r	λ	S.D	R	F	f-Taft
C_2	3.865±0.18	5.494±0.12	1.422	0.1108	0.9990	1901.37	0.049
C_{9a}	-0.957±0.07	-1.017±0.04	1.062	0.0409	0.9975	561.72	0.088
C_{10}	-3.944±0.26	-1.393±0.16	0.353	0.1547	0.9935	228.60	0.102
$C_{1'}$	5.765±1.49	14.460±0.95	2.508	0.9060	0.9910	161.80	0.155

d:

C atom	f	r	λ	S.D	R	F	f-Taft
C_2	4.099±0.31	6.001±0.20	1.464	0.1895	0.9980	765.70	0.076
C_{9a}	-0.892±0.08	-0.994±0.05	1.115	0.0463	0.9965	405.92	0.103
C_{10}	-4.507±0.24	-1.960±0.15	0.435	0.1430	0.9965	400.32	0.083
$C_{1'}$	5.201±1.28	13.957±0.81	2.684	0.7728	0.9930	203.93	0.137

n = 9;   λ = blending constant (r/f);   R = Multiple regression coefficient; F = F-Snedecor.

On using Reynolds' model **[Table 5]**, the C_2 gave excellent correlations for series **[a]**, while the series **[b, c and d]** gave moderately good correlations, with normal reaction constants for both a field (ρ_F) and a resonance (ρ_R), with blending constants λ in the range (2.032-2.137). The C_{9a}, gave moderately good correlations for series **[b, c and d]**, while the series **[a]** represent crude trends, with reverse reaction constants for both field and resonance, with a blending constants λ in the range (1.505-1.796). Both atoms C_{10} and $C_{1'}$, gave excellent correlations for all series,   with reverse reaction constants for both   field and resonance for C_{10}, and blending constants λ in the range (0.445-0.653), while the $C_{1'}$, with normal reaction constants for both field and resonance, with blending constants λ in the range (3.993-4.233).

Table 5. DSP Correlation analysis of ^{13}C SCS of C_2, C_{9a}, C_{10} and $C_{1'}$ for the series [a, b, c and d] on using Reynolds'model.

a:

C atom	ρ_F	ρ_R	λ	S.D	R	F	f-Taft
C_2	4.228±0.39	8.809±0.41	2.083	0.2417	0.9970	480.14	0.096
C_{9a}	-0.636±0.17	-1.141±0.18	1.796	0.1065	0.9685	45.53	0.303
C_{10}	-4.064±0.18	-2.355±0.19	0.580	0.1123	0.9975	559.78	0.069
$C_{1'}$	5.253±0.58	21.348±0.62	4.064	0.3603	0.9985	962.49	0.064

b:

C atom	ρ_F	ρ_R	λ	S.D	R	F	f-Taft
C_2	3.611±0.56	7.367±0.60	2.040	0.3519	0.9910	160.40	0.166
C_{9a}	-0.537±0.11	-0.950±0.12	1.771	0.0676	0.9813	79.07	0.234
C_{10}	-4.039±0.11	-2.639±0.12	0.653	0.0711	0.9990	1487.29	0.045
$C_{1'}$	5.487±0.37	21.979±0.39	4.005	0.2290	0.9995	2535.41	0.040

c:

C atom	ρ_F	ρ_R	λ	S.D	R	F	f-Taft
C_2	3.897±0.58	7.918±0.62	2.032	0.3616	0.9913	175.92	0.159
C_{9a}	-0.957±0.10	-1.441±0.11	1.505	0.0628	0.9935	236.71	0.135
C_{10}	-3.854±0.12	-1.716±0.13	0.445	0.0754	0.9985	972.43	0.049
$C_{1'}$	5.544±0.44	22.138±0.48	3.993	0.2778	0.9990	1749.95	0.048

d:

C atom	ρ_F	ρ_R	λ	S.D	R	F	f-Taft
C_2	4.088±0.58	8.735±0.63	2.137	0.3657	0.9925	203.37	0.147
C_{9a}	-0.913±0.13	-1.387±0.14	1.519	0.0810	0.9889	130.66	0.181
C_{10}	-4.390±0.17	-2.531±0.18	0.576	0.1065	0.9980	724.75	0.062
$C_{1'}$	5.035±0.59	21.315±0.63	4.233	0.3706	0.9985	896.63	0.066

n = 9; λ = blending constant (ρ_R/ρ_F); R = Multiple regression coefficient; F = F-Snedecor.

On using Taft model **[Table 6]**, The C_2 gave moderately good correlations for all the series, with normal reaction constants for both field (ρ_I) and resonance (ρ_R), with blending constants λ (1.808) with σ_R^o of series [a], and in the range (0.820-0.843) with σ_R^+ of the series [b,c and d]. The C_{9a}, gave an excellent correlation for series [a], and moderately good correlations for series **[b, c and d]**, with reverse reaction constants for both field and resonance, with a blending constants λ in the range (0.632-0.758) with σ_R^+ of the series **[a, b and d]** and (0.609) of series **[c]**. C_{10}, gave excellent correlations for all series, with reverse reaction constants for both a field and a resonance, with blending constants λ in the range (0.512-0.682) with σ_R^o scale. $C_{1'}$ gave moderately good correlations for all series, with normal reaction constants for both a field and a resonance, with blending constants λ in the range (3.069-3.160) with σ_R^o scale.

Table 6. DSP Correlation analysis of ^{13}C SCS of C_2, C_{9a}, C_{10} and $C_{1'}$ for the series [a, b, c and d] on using Taft's model.

a:

C atom	ρ_I	ρ_R	λ	S.D	R	F	f-Taft
C_2	4.580±0.67	8.279±0.72 [o]	1.808	0.4623	0.9884	129.12	0.184
C_{9a}	-0.603±0.04	-0.457±0.02 [+]	0.758	0.0298	0.9975	614.59	0.085
C_{10}	-3.929±0.22	-2.412±0.24 [o]	0.614	0.1502	0.9950	311.56	0.093
$C_{1'}$	6.437±1.45	19.829±1.57 [o]	3.080	0.9997	0.9879	122.42	0.178

n = 9; λ = blending constant (ρ_R/ρ_I); R = Multiple regression coefficient; F = F-Snedecor.
[o]: σ_I and σ_R^o parameters; [+]: σ_I and σ_R^+ parameters

b:

C atom	ρ_I	ρ_R	λ	S.D	R	F	f-Taft
C_2	3.439±0.41	2.831±0.17 [+]	0.823	0.2742	0.9945	266.04	0.129
C_{9a}	-0.506±0.05	-0.373±0.02 [+]	0.737	0.0361	0.9950	285.07	0.125
C_{10}	-3.925±0.17	-2.676±0.18 [o]	0.682	0.1169	0.9975	548.79	0.074
$C_{1'}$	6.629±1.29	20.521±1.39 [o]	3.096	0.8870	0.9910	166.26	0.153

c:

C atom	ρ_I	ρ_R	λ	S.D	R	F	f-Taft
C_2	3.706±0.46	3.039±0.19 [+]	0.820	0.3081	0.9940	243.34	0.135
C_{9a}	-0.907±0.12	-0.552±0.05 [o]	0.609	0.0791	0.9899	147.91	0.170
C_{10}	-3.653±0.17	-1.870±0.18 [o]	0.512	0.1175	0.9965	398.53	0.077
$C_{1'}$	6.720±1.38	20.627±1.50 [o]	3.069	0.9549	0.9899	145.45	0.164

d:

C atom	ρ_I	ρ_R	λ	S.D	R	F	f-Taft
C_2	3.930±0.56	3.319±0.24 [+]	0.843	0.3794	0.9920	188.65	0.153
C_{9a}	-0.856±0.10	-0.541±0.04 [+]	0.632	0.0666	0.9925	194.93	0.148
C_{10}	-4.231±0.19	-2.621±0.21 [o]	0.620	0.1315	0.9990	474.04	0.076
$C_{1'}$	6.250±1.52	19.748±1.64 [o]	3.160	1.0490	0.9864	109.27	0.186

On using modified Godfrey model **[Table 7]**, The C_2 gave moderately good correlations for all the series, with normal reaction constants for both field (ρ_I) and resonance ($\rho_{R,ST}$), with blending constants **(1-λ)** in the range (1.130-1.176). The C_{9a}, gave moderately good correlations for series **[b, c and d]**, while series **[a]** represent crude trends, with reverse reaction constants for both field and resonance, with blending constants **(1-λ)** in the range (0.896-1.000).

The C_{10}, gave excellent correlations for all the series, with reverse reaction constants for both field and resonance, with blending constants (1-λ) in the range (0.512-0.682). $C_{1'}$ gave excellent correlation constant for series **[b]**, while series gave moderately good correlations for series **[a, c and d]**, with normal reaction constants for both a field and a resonance, with blending constants **(1-λ)** in the range (1.990-2.051).

Table 7. DSP Correlation analysis of ^{13}C SCS effect of C_2, C_{9a}, C_{10} and $C_{1'}$for the series [a, b, c and d] on using Modified Godfrey model.

a:

C atom	ρ_I	$\rho_{R,ST}$	$1 - \lambda$	S.D	R	F	f-Taft
C_2	4.283±0.42	5.036±0.29	1.176	0.3090	0.9950	292.79	0.123
C_{9a}	-0.658±0.15	-0.638±0.11	0.969	0.1127	0.9649	40.28	0.321
C_{10}	-3.691±0.13	-1.470±0.09	0.398	0.0946	0.9980	790.71	0.058
$C_{1'}$	6.025±0.94	12.019±0.65	1.995	0.6932	0.9940	257.81	0.123

b:

C atom	ρ_I	$\rho_{R,ST}$	$1 - \lambda$	S.D	R	F	f-Taft
C_2	3.700±0.55	4.179±0.38	1.130	0.4039	0.9879	121.00	0.190
C_{9a}	-0.541±0.10	-0.541±0.07	1.000	0.0710	0.9798	71.43	0.246
C_{10}	-3.676±0.10	-1.632±0.07	0.444	0.0700	0.9990	1534.93	0.044
$C_{1'}$	6.193±0.78	12.426±0.54	2.006	0.5718	0.9965	404.27	0.099

c:

C atom	ρ_I	$\rho_{R,ST}$	$1 - \lambda$	S.D	R	F	f-Taft
C_2	3.975±0.58	4.499±0.40	1.132	0.4240	0.9884	127.09	0.186
C_{9a}	-0.932±0.09	-0.835±0.06	0.896	0.0630	0.9935	235.07	0.135
C_{10}	-3.422±0.18	-1.135±0.12	0.332	0.1303	0.9955	323.61	0.086
$C_{1'}$	6.280±0.86	12.499±0.59	1.990	0.6290	0.9955	338.97	0.108

d:

C atom	ρ_I	$\rho_{R,ST}$	$1 - \lambda$	S.D	R	F	f-Taft
C_2	4.220±0.58	4.952±0.40	1.174	0.4247	0.9899	149.99	0.171
C_{9a}	-0.886±0.11	-0.805±0.08	0.908	0.0833	0.9879	123.46	0.186
C_{10}	-3.972±0.13	-1.592±0.09	0.401	0.0966	0.9985	881.37	0.056
$C_{1'}$	5.843±1.00	11.981±0.65	2.051	0.7334	0.9935	226.73	0.130

n = 9; $(1-\lambda)$ = blending constant $(\rho_{R,ST}/\rho_I)$; R = Multiple regression coefficient; F = F-Snedecor.

When the obtained DSP regression coefficients for the C_2 values were compared in the series [a, b and c] [Tables 4-7], both field and resonance values are the highest in the open-chain chalcones series [d] and the smallest in the tetralone series [b]. The corresponding field and resonance values obtained for the five-membered series [a] and the series [d], are very close to those obtained for the substituent effects in the more planar compounds [a] and [d], and the lower one in the least planar compounds [b and c]. Since, using all the four sets of constants (modified Swain-Lupton, Reynolds, Taft and modified Godfrey models) the respective field and resonance regression coefficients follow the same decreasing order of series [a = d > c > b] corresponding to the relative degree of planarity of the four series, the field and resonance values apparently seem to be appropriate indicators of planarity of the investigated cinnamoyl enones. On the other hand, it is worth mentioning that, although in statistical terms the correlation of substituent effects with the C_{9a} is rather good in all the four series, the regression coefficient ρ values are very low and do not indicate the difference in stereochemistry of the four series.

In accord with the earlier results [7], sensitivity of the C_{10} to the substituent resonance effect is smaller than that of C_2 in all the four series. On the other hand, the respective the field values are very similar (**Tables 4-7**). This latter observation can exist in the s-cis system which stabilizes the dipolar from even if the degree of planarity of the enone moiety is significant [6]. This also might be the reason for the observation that the DSP analysis of C_2 of the four series (modified Swain-Lupton, Reynolds, Taft and modified Godfrey models) resulted in higher a field than a resonance values in all the four series. Similar results were obtained for DSP analysis of the carbonyl stretching wave numbers of series [a, b and c] [7] and that of the C_2 of E-2-(4'-X-benzylidene)-1-cyclohexanones [6].

4. Models performance assessment of MSP and DSP models:

The statistical parameter **f-Taft (SD/RMS)** was used to judge the quality for these models. The results were tabulated in **[Table 8]**. The modified Swain-Lupton model is the best one for **C_2** SCS effect for all series. For **C_{9a}**, both models σ^{13} and Hammett, are the best for series **[a]**, while modified Swain-Lupton model is the best one for both series **[c and d]**, but for series **[d]** both models Hammett and modified Swain-Lupton model have the same quality. For **C_{10}**, both modified Swain-Lupton and Reynolds models have the same quality for series [a], while both Reynolds and modified Godfrey models have the same quality for series **[b]**, Reynolds model is the best for series **[c]**, while Godfrey model is the best one for series **[d]**. For **$C_{1'}$**, Reynolds model is the best one for the all series.

Table 8. A comparison of the statistical parameter f-Taft (SD/RMS) of MSP and DSP models:

Series	C atom	σ^{13}	Hammett	M. Swain	Reynolds	Taft	M. Godfrey
A	C_2	0.134	0.140	0.084	0.096	0.184 [o]	0.123
	C_{9a}	0.118	0.120 *	0.157	0.303	0.085 [+]	0.321
	C_{10}	0.359	0.247	0.068	0.069	0.093 [o]	0.058
	$C_{1'}$	0.213	0.247 *	0.147	0.064	0.178 [o]	0.123
B	C_2	0.074	0.130	0.051	0.166	0.129 [+]	0.190
	C_{9a}	0.106	0.121	0.082	0.234	0.125 [+]	0.246
	C_{10}	0.355	0.230	0.062	0.045	0.074 [o]	0.044
	$C_{1'}$	0.229	0.265 *	0.166	0.040	0.153 [o]	0.099
C	C_2	0.087	0.129	0.049	0.159	0.135 [+]	0.186
	C_{9a}	0.163	0.084	0.088	0.135	0.170 [o]	0.135
	C_{10}	0.402	0.298	0.102	0.049	0.077 [o]	0.086
	$C_{1'}$	0.222	0.257 *	0.155	0.048	0.164 [o]	0.108
D	C_2	0.088	0.147	0.076	0.147	0.153 [+]	0.171
	C_{9a}	0.150	0.103	0.103	0.181	0.148 [+]	0.186
	C_{10}	0.377	0.260	0.083	0.062	0.076 [o]	0.056
	$C_{1'}$	0.212	0.241 *	0.137	0.066	0.186 [o]	0.130

M. Swain: Modified Swain-Lupton model;   **M. Godfrey: Modified Godfrey model;**   ***: σ^+ parameter ;**   **[+]: σ_I and σ_R^+ parameters;   [o]: σ_I and σ_R^o parameters.**

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التحليل الترابطي لتأثير المعوضات على الإزاحات الكيميائية لطيف الرنين النووي المغناطيسي 13-C لمركبات E-2-(‘4—Xبنزلدين)-1-اندونات,-تترالونات و –بنزوسبيرونات و الجالكونات.

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الملخص

درست الإزاحات الكيميائية لطيف الكربون –13 لذرات الكربون C_2 (C_α), C_{10}, C_{9a} (C_β) C_1, لمركبات E-2- (‘4—Xبنزلدين)-1-اندونات,-تترالونات , –بنزوسبيرونات و الجالكونات حيث:

$$X= H, NMe_2, OMe, Me, F, Cl, Br, CN, NO_2$$

في مذيب $CDCl_3$ درس التأثير باستخدام نوعين مختلفين من معامل المعوض: معامل المعوض أحادي الحد (MSP) (أنموذجات σ^{13} و هامت و براون–اوكوموتو) ومعامل المعوض ثنائي الحد (DSP) (أنموذجات سواين لبتون المعدل و رينولدز و تافت و كود فري المعدل) وأن كلا المعاملين (MSP) و (DSP) عكسا كثيرا مشاركة الرنين في التأثيرعلى الازاحة الكيميائية للذرة C_2 (C_α) , بينما ذرة C_{10} (C_β) عكست مبدئيا تأثير الحث لشطر الاينون في جميع السلاسل الأربع. تأثير الحث لم يكن واضحا كما هو الحال مع تأثير الرنين. وقد وجد بأن أنموذج DSP (لمعاملي الحث و الرنين) للمعوض على الازاحة الكيميائية لذرة C_2 (C_α) يمكن أن يستخدم مقياسا في دراسة هيئة أو استواء الآينونات في السلاسل الأربع. وأخيرا قيم أداء الأنموذجين (MSP) و (DSP).