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A Correlation Analysis Study of Substituent Effects by ^{13}C Nuclear Magnetic Resonance Spectrometry: Effect of Solvent on The Chemical Shift of C_α and C_β of Methyl Substituted Cinnamate.

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Abstract

The ^{13}C Substituent Chemical Shifts (SCS) for C_α and C_β atoms for the meta-**X**, meta-**CH₂X** and para-**CH₂X** substituted **methylcinnamate**(**X= H, Me, OMe, OPh, NMe₂, F, Cl, Br, I, CF₃, CN, NO₂**) in six different solvents (**EtOH, Me₂SO, Me₂CO, CDCl₃, CCl₄ and C₆H₆**), were modelled by two different types of substituent parameter: namely mono substituent parameter (**MSP**)(**Hammett's model**), and dual substituent parameter **DSP(modified Swain-Lupton model)**. For both C_β and C_α in meta-**X** series and the para-**CH₂X** series, the quality of Hammett's model and the modified Swain-Lupton model were found to be similar, while for C_β and C_α in the meta-**CH₂X** series the modified Swain-Lupton model is the best one. There is no significant difference between the reaction constants values in the same model, of the same atom of the same series in different solvents. The final conclusion, is that no solvent effect on **CH₂X** groups when studied by ^{13}C NMR spectrometry on using Hammett's and modified Swain-Lupton models.

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}C substituent 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:

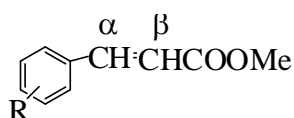
$$\text{SCS} = \rho\sigma \quad (1)$$

$$\text{SCS} = \rho_I\sigma_I + \rho_R\sigma_R \quad (2)$$

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.

The dependence of the Hammett reaction constant ρ on the solvent is often very marked and has been discussed since the earliest days of linear free energy relationship **LFER**. Indeed Hammett[1] predicted a linear relationship to the reciprocal of the dielectric constant. One of the most remarkable features of the Hammett equation is, in fact, its apparent wide applicability irrespective of choice of solvent. Thus σ values, based on the ionization of benzoic acids in water at 25 °C, have been used in the correlation analysis of the reactions carried out in a wide range of aqueous organic mixtures and also individual organic solvents, even as non-polar as dioxane or toluene[2] or gas-phase. In such correlations one or two of the chosen substituents may give deviate points and such observations are sometimes attributed to specific variations of sigma values with solvent.



meta R= X or CH₂X
para R= CH₂X

X= H, Me, OMe, OPh, NMe₂, F, Cl, Br, I, CF₃, CN, NO₂

Scheme 1.

The majority of styrene derivatives has only a limited solubility in aqueous or aqueous organic solvents, and there is no guarantee that inductive effects are solvent independent. Indeed, a solvent dependence study on the styrenes has shown that they are not. [10] As a possible alternative approach Happer et al.[11] decide to look at the effect of **meta**- and **para**-XCH₂-substituents on the ¹³C NMR chemical shifts of styrene derivative. In such systems, the resonance effects were present, and C-H hyperconjugations between the -CH₂- group

Recently, Ludwig et al.[3] have measured dissociation constants of 38 mono substituted benzoic acids in water and in six organic solvents by potentiometric titration. The sets of pK values were correlated with ordinary Hammett σ values derived from Exner's critical compilations[4]. As might be expected, potentially hydrogen-bonding substituents are especially prone to show deviations. Ptela et al.[5] submit the results of the above study principal components analysis and factor analysis produce sets new Hammett substituent constants, for the set of the six organic solvents.

A very large study of a rather different kind has been carried out by Hoefnagel and Wepster[6] on the dissociation constants of benzoic acids in water-organic solvent mixtures.

Somewhat related studies have been pursued by Fan and colleagues under the title of "The Effect of Hydrophobic-Lipophilic Interactions on Chemical Reactivity"[7-9].

and the aromatic nucleus being possible, but hoped that the effect of this on the overall chemical shifts might either be constant or proves proportional to the inductive effects of the substituents involved.

The system chosen for investigation was the **m-X**, **m-XCH₂** and **p-XCH₂**-substituted methylcinnamate (**Scheme 1**). The success or failure of the approach should be independent of the nature of any substituent(s) on the β -carbon, and the choice

of a single methoxy carbonyl group was based on convenience.[11]

In the course of obtaining the data for the C_β shifts, those for the α -carbons also become available. Brownlee and his co-workers[12] have reported that ^{13}C NMR chemical shifts for carbons of these types are also influenced by the electronic effect of substituents. The analysis of their C_α data using the DSP equation of Ehrenson et al.[13] led to negative values of ρ_I and ρ_R and these were interpreted in terms of a localized polarization of the side-chain arising from the direct field effect of the substituents. The explanation is not entirely satisfactory it adequately accounts for the negative values obtained for ρ_I . It does not

2. Procedure

The ^{13}C NMR chemical shifts of the α and β side-chain carbons of **meta-X**, **meta-CH₂X** and **para-CH₂X** substituted methylcinnamate [14] in six different solvents with “basis set” were modeled by different types of substituent parameter, DSP and SSP 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**

3. Results and Discussion

The chemical shift data for C_α and C_β for the **XCH₂**-substituted methylcinnamate are listed in **Tables 1** and **2** in the form of **SCS**, which represents the difference in chemical shift between the substituted and unsubstituted derivatives. They are also included for the purposes of comparison are data for the corresponding **meta-X**-substituted derivatives. The efficiency with which the electronic effect of **X** is relayed to C_α or C_β will depend on the mechanism by which it is relayed. In case of a direct field effect, the distance between **X** and the carbon under consideration should be

explain why ρ_R value should also be negative. The explanation advanced by Brownlee to account for negative values for ρ_R in side-chain containing a carbonyl group is not valid for ethenyl side-chains. However, ρ_R value is usually much lower in magnitude than ρ_I . For most substituents, the resonance contribution to the overall shifts is much less than the inductive one. The interposition of a **-CH₂**-group between the substituent and the π -system should eliminate any possibility of direct resonance interaction between the side-chain and **X**. It would be therefore expected to find that the ^{13}C NMR chemical shift for C_α like C_β should be proportional to the inductive effects of the substituents.

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 greater than **0.3** representing only crude trends [13].

the most important factor although the orientation of the **C-X** bond can play a significant part. On the other hand, if the effect involves the distortion of the σ - or π -electron system, (the distance is still important), the effectiveness of transmission should depend to the some extent on whether the **XCH₂** group is meta or para to the side-chain.

If we examine the data on this basis, we can see that the effect of substituent on the chemical shifts for C_α of the meta- and para-**XCH₂**-substituted derivatives are

relatively independent of whether the **XCH₂** is meta or para to the side-chain. This supports Brownlee's contention[12] that is the field effect which responsible for reverse substituent chemical shifts [i.e. The reverse nature of the effect arises because electron donating substituents set up a dipole that polarizes electron density a way from **C_α** (toward **C_β**), and electron releasing substituents set up a dipole that polarizes the electron density toward **C_α**][15]. It also suggested that any effect arising from differing orientations of the **C-X** bond is only minor one.

In the case of the **C_β** shifts, however, there are considerable differences in the efficiencies of transmission from the two positions. This being the case, the enhanced transmission of inductive effects from the para-position to the **β**-carbon of the side-chain cannot represent a **π**-inductive effect, which would involve merely the distortion of the **π**-system of the field effect of the substituent, but rather a resonance effect, involving a substituent-dependent variation in the extent of hyper conjugative interaction between **C_β** and the **CH₂**-group.

The ¹³C SCS for **C_α** and **C_β** atoms for the meta-**X**, meta-**CH₂X** and para-**CH₂X** substituted methylcinnamate in six different solvents (**EtOH**, **Me₂SO**, **Me₂CO**, **CDCl₃**, **CCl₄** and **C₆H₆**), were modeled by two different types of substituent parameters namely: mono substituent parameter **MSP (Hammett's model)**[16], and dual substituent parameter **DSP (modified Swain-Lupton model)**[7].

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.

For the meta-**X** series, on using Hammett's model, **C_β** gave an excellent correlations in all solvents except in both solvents **CDCl₃** and **CCl₄** which gave a moderately good, with normal reaction constants (**ρ**) in the range (**3.69-4.94**), (**Table 3**)

Table 1. ^{13}C SCS of C_β for meta- and para-substituted methylcinnamate in different solvents.

Substituent	EtOH	Me_2SO	Me_2CO	CDCl_3	CCl_4	C_6H_6
H	0.00	0.00	0.00	0.00	0.00	0.00
m-Me	-0.27	-0.25	-0.25	-0.28	-0.25	-0.23
m-OMe	0.19	0.33	0.27	0.32	0.14	0.20
m-OPh	0.88	0.92	0.99	0.66	0.69	0.76
m-NMe ₂	-0.83	-0.70	-0.76	-0.60	-0.71	-0.58
m-F	1.65	1.62	1.63	1.39	1.41	1.31
m-Cl	1.76	1.71	1.73	1.47	1.48	1.35
m-Br	1.72	1.68	1.76	1.49	1.49	1.30
m-I	1.52	1.38	1.46	1.29	1.33	1.16
m-CF ₃	2.30	2.20	2.28	2.01	2.01	1.74
m-CN	2.91	2.55	2.60	2.73	2.63	2.12
m-NO ₂	3.36	3.00	3.02	3.20	3.08	2.53
m-Et	-0.30	-0.27	-0.25	-0.31	-0.29	-0.22
m-CH ₂ OMe	0.24	0.17	0.10	0.18	0.07	0.11
m-CH ₂ OPh	0.35	0.42	0.39	0.40	0.35	0.37
m-CH ₂ NMe ₂	0.30	0.23	0.29	0.18	-0.10	0.07
m-CH ₂ F	0.68	0.58	0.57	0.67	0.65	0.54
m-CH ₂ Cl	0.68	0.63	0.68	0.74	0.72	0.59
m-CH ₂ Br	0.69	0.62	0.69	0.79	0.79	0.59
m-CH ₂ I	0.56	0.49	0.63	0.68	0.67	0.52
m-CH ₂ CN	1.00	0.79	0.88	1.22	1.17	0.90
<i>p</i> -Me	-1.13	-1.09	-1.19	-1.10	-1.04	-0.99
<i>p</i> -Et	-1.08	-1.07	-1.17	-1.10	-1.01	-0.95
<i>p</i> -CH ₂ OMe	-0.14	-0.25	-0.26	-0.13	-0.27	-0.24
<i>p</i> -CH ₂ OPh	0.00	0.05	0.04	0.02	-0.01	0.03
<i>p</i> -CH ₂ NMe ₂	-0.08	-0.33	-0.35	-0.37	-0.52	-0.41
<i>p</i> -CH ₂ F	0.54	0.57	0.52	0.56	0.53	0.46
<i>p</i> -CH ₂ Cl	0.55	0.58	0.58	0.65	0.61	0.48
<i>p</i> -CH ₂ Br	0.59	0.54	0.53	0.66	0.64	0.53
<i>p</i> -CH ₂ CN	0.64	0.40	0.52	0.86	0.81	0.58

In a comparison with meta- CH_2X series, which gave only crude trends with normal reaction constants in the range (3.31-4.66), (Table 4). On using modified Swain-Lupton model, for the meta- X series, C_β gave an excellent correlations in all solvents except in both solvents CDCl_3 and CCl_4 which gave a moderately good with normal reaction constants for field (f) and resonance (r), with blending constants λ (ρ_r/ρ_f) in the range (0.348-0.381), (Table 5). In a comparison with meta- CH_2X series, C_β gave good correlations in all solvents except in CCl_4 and C_6H_6 which

gave crude trends, (Table 6). With lower field effects (f) and higher resonance effects (r) in all solvents, with blending constants (λ) in the range (1.556-3.666). The lowering in the field effect may be attributed to the long distance from the substituent X , in the meta- CH_2X series, to C_β , while the higher resonance effect may be attributed to the resonance structures of some CH_2X substituents ($\text{X} = \text{NMe}_2, \text{OMe}, \text{OPh}$ and CN) with the aromatic ring, which enhance the resonance effect of C_β (Scheme 2).

Table 2. ^{13}C SCS of C_α for meta- and para-substituted methylcinnamate in different solvents.

Substituent	EtOH	Me_2SO	Me_2CO	CDCl_3	CCl_4	C_6H_6
H	0.00	0.00	0.00	0.00	0.00	0.00
m-Me	0.23	0.10	0.15	0.19	0.24	0.29
m-OMe	-0.01	-0.06	-0.01	-0.14	0.09	0.11
m-OPh	-0.77	-0.82	-0.78	-0.72	-0.59	-0.76
m-NMe ₂	1.33	1.21	1.34	1.14	1.33	1.48
m-F	-1.55	-1.46	-1.43	-1.38	-1.38	-1.45
m-Cl	-1.70	-1.63	-1.65	-1.70	-1.57	-1.75
m-Br	-1.86	-1.71	-1.75	-1.80	-1.63	-1.80
m-I	-1.89	-1.67	-1.77	-1.85	-1.75	-1.82
m-CF ₃	-1.95	-1.77	-1.76	-1.85	-1.78	-1.96
m-CN	-2.72	-2.29	-2.37	-2.85	-2.59	-2.74
m-NO ₂	-2.77	-2.44	-2.50	-2.93	-2.70	-2.88
m-Et	0.25	0.14	0.25	0.30	0.31	0.44
m-CH ₂ OMe	-0.16	-0.11	-0.04	-0.19	0.00	-0.03
m-CH ₂ OPh	-0.22	-0.20	-0.19	-0.37	-0.23	-0.26
m-CH ₂ NMe ₂	-0.23	-0.15	-0.16	-0.14	0.16	0.19
m-CH ₂ F	-0.53	-0.55	-0.45	-0.70	-0.58	-0.55
m-CH ₂ Cl	-0.65	-0.59	-0.63	-0.74	-0.72	-0.67
m-CH ₂ Br	-0.72	-0.64	-0.70	-0.83	-0.74	-0.79
m-CH ₂ I	-0.58	-0.59	-0.64	-0.79	-0.66	-0.73
m-CH ₂ CN	-0.90	-0.69	-0.78	-1.19	-1.02	-1.00
<i>p</i> -Me	0.06	0.03	-0.01	0.01	-0.04	0.05
<i>p</i> -Et	0.10	-0.01	0.09	0.04	0.00	0.10
<i>p</i> -CH ₂ OMe	-0.36	-0.30	-0.20	-0.35	-0.21	-0.21
<i>p</i> -CH ₂ OPh	-0.23	-0.36	-0.37	-0.43	-0.33	-0.41
<i>p</i> -CH ₂ NMe ₂	-0.41	-0.24	-0.22	-0.23	-0.12	-0.10
<i>p</i> -CH ₂ F	-0.66	-0.62	-0.60	-0.81	-0.76	-0.73
<i>p</i> -CH ₂ Cl	-0.78	-0.64	-0.72	-0.91	-0.79	-0.78
<i>p</i> -CH ₂ Br	-0.83	-0.73	-0.79	-0.92	-0.89	-0.84
<i>p</i> -CH ₂ CN	-0.96	-0.73	-0.79	-1.25	-1.16	-1.09

Table 3. Correlation analysis of ^{13}C SCS of C_β for meta-substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	f-Taft	F
EtOH	4.964±0.22	0.1914	0.9899	0.108	494.73
Me_2SO	4.443±0.18	0.1555	0.9920	0.095	604.14
Me_2CO	4.561±0.19	0.1665	0.9910	0.099	551.56
CDCl_3	4.466±0.24	0.2080	0.9849	0.130	338.74
CCl_4	4.450±0.23	0.1931	0.9874	0.123	390.53
C_6H_6	3.694±0.14	0.1189	0.9930	0.089	709.32

$n=12$; r = linear correlation coefficient; F = F-Snedecor.

Table 4. Correlation analysis of ^{13}C SCS of C_β for meta-XCH₂-substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	f-Taft	F
EtOH	3.916±0.83	0.2296	0.8585	0.409	22.40
Me_2SO	3.179±0.84	0.2330	0.8012	0.478	14.34
Me_2CO	3.458±0.90	0.2484	0.8068	0.469	14.92
CDCl_3	4.451±1.00	0.2787	0.8432	0.442	19.65
CCl_4	4.466±1.10	0.2962	0.8282	0.489	17.51

C ₆ H ₆	3.310±0.84	0.2318	0.8142	0.481	15.17
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n=10; r= linear correlation coefficient; F= F-Snedecor.

Table 5. DSP correlation analysis of ¹³C SCS of C_β for meta-substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	F	r	λ	S.D	R	f-Taft	F
EtOH	4.828±0.25	1.839±0.15	0.381	0.1565	0.9940	0.088	372.56
Me ₂ SO	4.440±0.24	1.544±0.14	0.348	0.1452	0.9935	0.089	345.13
Me ₂ CO	4.521±0.24	1.618±0.14	0.358	0.1501	0.9935	0.090	341.15
CDCl ₃	4.399±0.32	1.607±0.19	0.365	0.1966	0.9884	0.130	190.70
CCl ₄	4.302±0.26	1.671±0.16	0.389	0.1627	0.9920	0.103	277.44
C ₆ H ₆	3.688±0.18	1.288±0.10	0.349	0.1086	0.9950	0.081	426.81

n=12; λ= blending constant (ρ_r/ρ_f); R= Multiple regression coefficient; F= F-Snedecor.

Table 6. DSP correlation analysis of ¹³C SCS of C_β for meta-XCH₂-substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	F	r	λ	S.D	R	f-Taft	F
EtOH	2.090±0.66	4.405±0.73	2.107	0.1253	0.9649	0.223	47.53
Me ₂ SO	1.303±0.68	4.198±0.76	3.222	0.1298	0.9503	0.266	32.50
Me ₂ CO	1.299±0.54	4.762±0.60	3.666	0.1031	0.9731	0.195	62.98
CDCl ₃	2.412±0.96	4.946±1.07	2.051	0.1825	0.9439	0.290	28.74
CCl ₄	2.804±1.30	4.363±1.45	1.556	0.2477	0.8989	0.409	14.73
C ₆ H ₆	1.686±0.86	3.845±0.96	2.280	0.1637	0.9236	0.340	20.27

n=10; λ= blending constant (ρ_r/ρ_f); R= Multiple regression coefficient; F= F-Snedecor.

C_α of the meta-X series, on using Hammett's model, gave moderately good correlations in all solvents with reverse reaction constants in the range (-5.03)–(-4.22), (Table 7). In a comparison with meta-CH₂X series, which gave only crude trends in all solvents with reverse reaction constants in the range (-4.60)–(-3.02), (Table 8). On using a modified Swain-Lupton model, C_α of the meta-X series gave a moderately good correlations

in all solvents, (Table 9), with a reverse reaction constants for a field (f) and a resonance (r) and blending constants (λ) in the range (0.425-0.504), while the C_α, of the meta-CH₂X series gave moderately good correlations in all solvents except in CCl₄ and C₆H₆ solvents which gave only crude trends with reverse reaction constants for both a field and a resonance, (Table 10), with blending constants in the range (1.395-2.122).

Table 7. Correlation analysis of ^{13}C SCS of C_α for meta-substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	f-Taft	F
EtOH	-4.828±0.36	0.3051	0.9737	0.182	184.06
Me_2SO	-4.219±0.33	0.2814	0.9711	0.188	165.31
Me_2CO	-4.412±0.36	0.3097	0.9680	0.202	149.23
CDCl_3	-4.677±0.49	0.4213	0.9492	0.259	90.580
CCl_4	-4.648±0.35	0.2976	0.9731	0.190	179.28
C_6H_6	-5.026±0.36	0.3100	0.9752	0.184	193.25

n=12; r= linear correlation coefficient; F= F-Snedecor.

Table 8. Correlation analysis of ^{13}C SCS of C_α for meta- XCH_2 -substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	f-Taft	F
EtOH	-3.731±0.71	0.1957	0.8820	0.383	27.97
Me_2SO	-3.020±0.58	0.1622	0.8769	0.364	26.68
Me_2CO	-3.404±0.75	0.2078	0.8491	0.438	20.66
CDCl_3	-4.476±0.95	0.2630	0.8579	0.412	22.30
CCl_4	-4.345±0.99	0.2752	0.8402	0.493	19.17
C_6H_6	-4.597±1.06	0.2949	0.8367	0.514	18.71

n=10; r= linear correlation coefficient; F= F-Snedecor.

Table 9. DSP correlation analysis of ^{13}C SCS of C_α for meta-substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	F	r	Λ	S.D	R	f-Taft	F
EtOH	-4.514±0.43	-1.942±0.26	0.430	0.2665	0.9823	0.159	122.64
Me_2SO	-3.963±0.41	-1.682±0.25	0.425	0.2548	0.9788	0.170	102.39
Me_2CO	-4.098±0.45	-1.798±0.27	0.439	0.2779	0.9767	0.181	94.37
CDCl_3	-4.138±0.59	-2.084±0.35	0.504	0.3644	0.9659	0.224	62.73
CCl_4	-4.249±0.39	-1.951±0.23	0.459	0.2408	0.9844	0.154	140.10
C_6H_6	-4.592±0.40	-2.110±0.24	0.459	0.2451	0.9859	0.145	158.09

n=12; λ = blending constant (ρ_r/ρ_f); R= Multiple regression coefficient; F= F-Snedecor.

Table 10. DSP correlation analysis of ^{13}C SCS of C_α for meta- XCH_2 -substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	F	r	λ	S.D	R	f-Taft	F
EtOH	-2.125±0.47	-3.999±0.52	1.882	0.0892	0.9798	0.175	83.12
Me_2SO	-1.855±0.53	-3.037±0.59	1.637	0.1003	0.9607	0.225	41.87
Me_2CO	-1.817±0.63	-3.854±0.70	2.122	0.1194	0.9586	0.251	39.95
CDCl_3	-2.674±0.97	-4.587±1.08	1.715	0.1849	0.9413	0.289	27.17
CCl_4	-2.879±1.23	-4.015±1.37	1.395	0.2346	0.9017	0.421	15.22

C ₆ H ₆	-2.955±1.30	-4.387±1.44	1.485	0.2463	0.9039	0.429	15.65
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n=10; λ = blending constant (ρ_r/ρ_f); R= Multiple regression coefficient; F= F-Snedecor.

In comparison, ρ for meta-**X** series are greater than that of the meta-**CH₂X** series, which may be attributed to the greater distance between the meta-**CH₂X** substituent and C _{α} , while the ρ values are greater for C _{α} and this may be attributed to the resonance structures of some **CH₂X** substituents (**X**= NMe₂, OMe, OPh and CN) with the aromatic ring, which enhance the resonance effect of C _{α} (Scheme 2).

For the para-**CH₂X** series, on using Hammett's model, C _{β} , gave only crude trends correlations with normal reaction constants in the range (4.41-5.40)(Table 11). On using a modified Swain-Lupton model, a crude trends correlations were

4. Model performance assessment and the effect of solvent on **CH₂X** groups

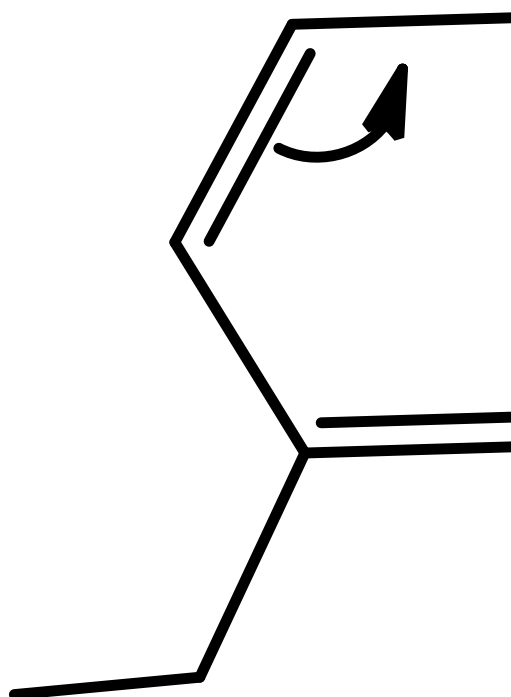
For both C _{β} and C _{α} for meta-**X** series and the para-**CH₂X** series, the quality of Hammett's model and the modified Swain-Lupton model were found to be similar, while for C _{β} and C _{α} of the the meta-**CH₂X** series the modified Swain-Lupton model is the best one.

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also obtained with normal reaction constants for both a field and a resonance, with blending constants λ in the range (1.673-2.397) Table 12.

On using Hammett's model, C _{α} gave moderately good correlations in all solvents except in CCl₄ and C₆H₆ solvents which gave crude trends, with reverse reaction constants in the range (-2.15)-(-3.00), Table 13. A modified Swain-Lupton model, also gave moderately good correlations in all solvents except in CCl₄ and C₆H₆ solvents which gave crude trends also, Table 14, and reverse reaction constants for both a field and a resonance, with blending constants λ in the range (1.148-1.993).

There is no significant difference between reaction constants values in the same model, of the same atom in the same series in different solvents. The final conclusion, is that no solvent effect on **CH₂X** groups on using Hammett's and modified Swain-Lupton models.



Scheme 2.

Table 11. Correlation analysis of ^{13}C SCS of C_β for para-XCH₂-substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_p	S.D	r	f-Taft	F
EtOH	5.002±0.68	0.2487	0.9418	0.382	54.74
Me ₂ SO	4.625±0.85	0.3126	0.8994	0.493	29.63
Me ₂ CO	4.998±0.85	0.3129	0.9116	0.462	34.54
CDCl ₃	5.401±0.75	0.2768	0.9381	0.392	51.55
CCl ₄	5.119±0.80	0.2952	0.9236	0.434	40.69
C ₆ H ₆	4.414±0.73	0.2699	0.9165	0.455	36.75

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

Table 12. DSP correlation analysis of ^{13}C SCS of C_β for para-XCH₂-substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	f	r	λ	S.D	R	f-Taft	F
EtOH	3.043±1.06	7.297±1.20	2.397	0.2019	0.9675	0.310	43.87
Me ₂ SO	2.839±1.56	6.717±1.76	2.366	0.2964	0.9236	0.467	17.37
Me ₂ CO	3.042±1.52	7.288±1.71	2.396	0.2879	0.9370	0.425	21.53
CDCl ₃	4.032±1.43	7.005±1.62	1.737	0.2720	0.9492	0.385	27.30
CCl ₄	3.906±1.58	6.536±1.78	1.673	0.2994	0.9333	0.440	20.19
C ₆ H ₆	3.008±1.37	6.060±1.54	2.015	0.2599	0.9333	0.438	20.24

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

Table13. Correlation analysis of ^{13}C SCS of C_α for para-XCH₂-substituted methylcinnamate in different solvents on using Hammett's model.

Solvent	ρ_p	S.D	R	f-Taft	F
EtOH	-2.919±0.16	0.0600	0.9894	0.127	320.38
Me ₂ SO	-2.151±0.27	0.1011	0.9476	0.207	61.32
Me ₂ CO	-2.392±0.38	0.1403	0.9214	0.274	39.31
CDCl ₃	-3.256±0.47	0.1719	0.9349	0.250	48.57
CCl ₄	-2.971±0.52	0.1924	0.9066	0.332	32.28
C ₆ H ₆	-3.000±0.53	0.1944	0.9066	0.323	32.24

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

Table 14. DSP correlation analysis of ^{13}C SCS of C_α for para-XCH₂-substituted methylcinnamate in different solvents on using modified Swain-Lupton model.

Solvent	F	r	λ	S.D	R	f-Taft	F
EtOH	-2.497±0.28	-3.413±0.31	1.367	0.0523	0.9930	0.111	212.04
Me ₂ SO	-1.663±0.53	-2.723±0.59	1.640	0.0998	0.9560	0.205	32.01
Me ₂ CO	-1.641±0.71	-3.270±0.80	1.993	0.1355	0.9376	0.265	21.83
CDCl ₃	-2.838±0.96	-3.745±1.08	1.320	0.1817	0.9376	0.264	21.85
CCl ₄	-2.782±1.09	-3.193±1.23	1.148	0.2071	0.9072	0.332	13.95
C ₆ H ₆	-2.443±1.07	-3.653±1.21	1.495	0.2038	0.9121	0.338	14.85

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

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دراسة التحليل الترابطي لتأثير المعوض باستخدام مطيافية الرنين النووي المغناطيسي C-13 .
تأثير المذيب على الازاحات الكيماوية لذرتي C_{α} و C_{β} لمثيل السناميت المعوض.

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البصرة- العراق

الملخص

درست الإزاحات الكيماوية لمعوض الكربون-13 لذرتي الكربون (C_{α} , C_{β}) للمعوضات-*meta*, *para*- CH_2 , *meta*- CH_2X , للمثيل سناميت حيث:

$X = H, Me, OMe, OPh, NMe_2, F, Cl, Br, I, CF_3, CN, NO_2$

في ستة مذيبات مختلفة ($EtOH, Me_2SO, Me_2CO, CDCl_3, CCl_4, C_6H_6$) درست باستخدام نوعين مختلفين من معامل المعوض: معامل المعوض أحادي الحد (MSP) (أنموذج هامت) ومعامل المعوض ثنائي الحد (DSP) (أنموذج سواين لبتون المعدل) جودة أنموذجي هامت و سواين- لبتون المعدل كانا متماثلين لكلا ذرتي الكربون (C_{α} , C_{β}) في السلسلتين و بينما كان أنموذج سواين - لبتون المعدل, الأفضل لسلسلة *meta*- CH_2X .

لا توجد اختلافات جوهرية بين قيم ثوابت التفاعل لأنموذج نفسه و للذرة لنفسها و السلسلة نفسها في مذيبات مختلفة. الاستنتاج النهائي لا يوجد تأثير للمذيب على مجاميع المدروسة بمطيافية الرنين النووي المغناطيسي ($^{13}C-NMR$) باستخدام أنموذجي هامت و سواين - لبتون المعدل.