
A Correlation Analysis Study of Substituent Effects by ^{13}C Nuclear Magnetic Resonance : Effect of Solvent on The Chemical Shift of C_α and C_β of meta- and para-X-substituted Styrenes.

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Abstract

The ^{13}C Substituent Chemical Shifts (SCS) for C_α and C_β atoms for the meta- and para-X-substituted **styrenes** ($\text{X} = \text{H, NMe}_2, \text{OMe, Me, F, Cl, Br, CF}_3, \text{CO}_2\text{Me, COMe, CN, NO}_2$) in seven different solvents (**75%EtOH-D₂O, 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, Reynolds' and Taft models)**. 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 C_α and C_β of styrene on using Hammett, modified Swain-Lupton, Reynolds and Taft models.

Keywords: Correlation analysis; ^{13}C SCS; Solvent effect; Hammett's Model; Modified Swain-Lupton Model; Reynolds model; Taft model; C_α and C_β of meta- and para-X-substituted Styrenes; Transmission of substituent Effects.

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.

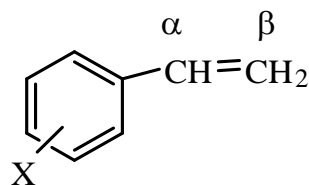
The dependence of the Hammett reaction constant ρ on the solvent is often very marked and has been discussed since the earliest days of linear free energy relationship LFER. Indeed (Hammett, 1937) predicted a linear relationship to the reciprocal of the dielectric constant. One of the most remarkable 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 $^{\circ}\text{C}$,

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 (Hancock and Westmoreland, 1958) 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.

Ludwig *et al.*, (Ludwig *et al.*, 1986) have measured dissociation constants of 38 mono substituted benzoic acids in water and in six organic solvents by potentiometric titration. The sets of pKa values were correlated with ordinary Hammett σ values derived from Exner's critical compilations (Chapman and Shorter, 1978). As might be expected, potentially hydrogen-bonding substituents are especially prone to show deviations. (Ptela *et al.*, 1986) 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, 1989) 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" (Jiang *et al.*, 1985; Jiang *et al.*, 1984; Fan *et al.*, 1985).



X= H, NMe₂, OMe, Me, F, Cl, Br, CF₃, CO₂Me, COMe, 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 (Happer, 1982). As a possible alternative approach (Happer and Steenson, 1983) 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 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 **meta-** and **para-X-**substituted styrene (**Scheme 1**). In the course of obtaining the data for the C_β shifts, those for the C_α also become available. Brownlee and his co-workers (Brownlee *et al.*, 1981). have reported that ¹³C 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.*, 1985) 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. Solvent dependence of SCS were observed for many substituents. but these could not be resolved with certainly into individual dependence on σ and ρ. It was tentatively proposed that in the meta-series, changes in SCS reflected changes in ρ. Such conclusion led to results that were inconsistent with one of the basic assumptions of the other groups, that the σ_I values for halogeno substituents show little variation with solvent, since it predicted that these were ca. 20-30% lower in non-polar ones. In most of the systems considered, substituent chemical shifts for halogeno-substituted compounds showed relatively small variations with solvent. The observed substituent effects appeared to result, the main, from localized polarization of the side-chain π system, induced by the field effect of the substituent. The effect of solvent was more pronounced than that observed in the styrene C_α data, but the pattern differed from that for C_β. It would be therefore expected to find that the ¹³C NMR chemical shift for C_α like C_β should be proportional to the inductive effects of the substituents. 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 in different solvents.

Procedure

The ^{13}C NMR chemical shifts of the α and β side-chain carbons of **meta-** and **para-X-** substituted styrenes (Happer and Steenson, 1985) in seven 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 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 (Ehrenson *et al.*,1973).

Results and Discussion

The chemical shift data for C_α and C_β for the meta- and para-X-substituted styrene are listed in **Tables 1- 4**, in the form of **SCS**, which represents the difference in chemical shift between the substituted and unsubstituted 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 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 **X** 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-X-substituted derivatives are relatively independent of whether the **X** is meta or para to the side-chain. This supports Brownlee's contention (Bromilow *et al.*,1981) 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 (Craik *et al.*,1983). 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.

The ^{13}C SCS for C_α and C_β atoms for the meta- and para-**X**-substituted styrene in seven different solvents (**75%EtOH-D₂O**, **EtOH**, **Me₂SO**, **Me₂CO**, **CDCl₃**, **CCl₄** and **C₆H₆**)(Happer and Steenson, 1985), were modeled by two different types of substituent parameters namely: mono substituent parameter **MSP (Hammett's model)**(Hansch *et al.*,1991), and dual substituent parameter **DSP (modified Swain-Lupton)**(Hansch *et al.*,1991), **Reynolds**(Reynolds *et al.*,1983) and **Taft** (Bromilo *et al.*,1979) **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 (Al-Shawi,1998), “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) (Craik and Brownlee, 1982).

Table 1. ^{13}C SCS of C_β in meta-X-substituted styrenes in different solvents.

Substituent	75%EtOH	EtOH	Me ₂ SO	Me ₂ CO	CDCl ₃	CCl ₄	C ₆ H ₆
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NMe ₂	-0.42	-0.65	-0.68	-0.76	-0.44	-0.68	-0.59
OMe	0.46	0.22	0.31	0.24	0.28	0.12	0.24
Me	-0.18	-0.24	-0.23	-0.26	-0.20	-0.24	-0.22
F	1.72	1.65	1.76	1.73	1.40	1.44	1.37
Cl	1.89	1.82	1.93	1.90	1.55	1.57	1.55
Br	1.97	1.90	1.91	1.95	1.61	1.67	1.51
CF ₃	2.48	2.39	2.40	2.32	2.04	2.17	1.97
CO ₂ Me	1.81	1.67	1.54	1.57	1.34	1.28	1.34
COMe	1.85	1.73	1.44	1.46	1.50	1.45	1.31
CN	3.28	3.16	2.92	2.92	2.84	2.90	2.46
NO ₂	3.69	3.56	3.41	3.50	3.31	3.32	2.87

Table 2. ^{13}C SCS of C_β in para-X-substituted styrenes in different solvents.

Substituent	75%EtOH	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	0.00
NMe_2	-4.08	-4.27	-5.03	-4.90	-4.44	-4.25	-4.38
OMe	-2.14	-2.31	-2.48	-2.44	-2.20	-2.18	-2.24
Me	-1.05	-1.03	-1.13	-1.08	-1.01	-1.02	-1.04
F	0.01	-0.11	-0.11	-0.04	-0.26	-0.17	-0.33
Cl	1.09	0.97	1.00	1.02	0.68	0.76	0.64
Br	1.21	1.09	1.07	1.05	0.78	0.86	0.69
CF_3	3.31	3.13	3.23	3.09	2.73	2.74	2.60
CO_2Me	3.39	3.14	3.12	2.95	2.68	2.45	2.52
COMe	3.58	3.31	3.05	2.96	2.93	2.74	2.59
CN	4.57	4.24	4.19	4.05	3.92	3.78	3.37
NO_2	5.43	5.11	5.22	5.08	4.79	4.54	4.18

Table 3. ^{13}C SCS of C_α in meta-X-substituted styrenes in different solvents.

Substituent	75%EtOH	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	0.00
NMe_2	0.77	0.88	0.91	1.01	0.77	0.94	1.12
OMe	-0.08	-0.05	-0.14	-0.01	-0.07	-0.09	-0.02
Me	0.11	0.11	0.09	0.07	0.06	0.09	0.13
F	-1.18	-1.12	-1.12	-1.13	-1.09	-1.02	-1.32
Cl	-1.35	-1.36	-1.37	-1.42	-1.30	-1.30	-1.58
Br	-1.45	-1.44	-1.47	-1.47	-1.40	-1.41	-1.65
CF_3	-1.42	-1.40	-1.40	-1.43	-1.23	-1.36	-1.68
CO_2Me	-0.94	-1.01	-1.01	-0.92	-1.01	-0.88	-1.11
COMe	-0.99	-0.92	-0.82	-0.77	-0.95	-0.84	-0.99
CN	-2.14	-2.14	-2.00	-2.01	-2.05	-2.03	-2.37
NO_2	-2.16	-2.11	-1.95	-1.99	-2.16	-2.14	-2.50

Table 4. ^{13}C SCS of C_α in para-X-substituted styrenes in different solvents.

Substituent	75%EtOH	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	0.00
NMe_2	-0.07	-0.05	-0.10	-0.07	-0.36	-0.29	0.00
OMe	-0.61	-0.69	-0.55	-0.59	-0.67	-0.68	-0.56
Me	-0.13	-0.18	-0.18	-0.15	-0.20	-0.19	-0.12
F	-1.22	-1.27	-1.23	-1.25	-1.20	-1.25	-1.36
Cl	-1.31	-1.31	-1.27	-1.30	-1.22	-1.25	-1.40
Br	-1.26	-1.26	-1.27	-1.23	-1.14	-1.17	-1.34
CF_3	-1.40	-1.41	-1.31	-1.43	-1.29	-1.30	-1.57
CO_2Me	-1.02	-0.97	-1.00	-0.89	-0.87	-0.81	-1.04
COMe	-1.04	-0.97	-0.94	-0.91	-1.02	-0.89	-1.04
CN	-1.56	-1.59	-1.42	-1.47	-1.51	-1.50	-1.78
NO_2	-1.98	-1.89	-1.75	-1.82	-1.92	-1.91	-2.23

For both meta- and para-X series, on using Hammett's model, C_β gave a moderately good correlation in all solvents, with normal reaction constants (ρ) in the range (4.10-5.04) and (5.38-6.46) respectively, (Table 5 and 6). Modified Swain-Lupton model gave a moderately good correlation in all solvents, for both series meta- and para-X-series, with normal field and resonance effects with blending constant (λ) in the range (0.28-0.31) and (1.09-1.19) respectively, (Table 7

and 8). While, Reynolds and Taft models both of them gave an excellent correlation with C_β in all solvents, for both meta- and para-X-series, except the last series in C_6H_6 solvent which gave a moderately good correlation, with normal field and resonance effects, with blending constant (λ) in the range (0.42-0.50) and (1.67-1.89) of the Reynolds model (Table 9 and 10), and (0.36-0.45) and (1.48-1.65) of the Taft model (Table 11 and 12), respectively.

Table 5. Correlation analysis of C_β in meta-X-substituted styrenes in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	F	f-Taft
75%EtOH	5.039±0.23	0.2013	0.9894	468.19	0.101
EtOH	5.071±0.24	0.2073	0.9889	447.12	0.108
Me ₂ SO	4.864±0.26	0.2225	0.9864	357.25	0.120
Me ₂ CO	4.983±0.24	0.2067	0.9884	434.35	0.111
CDCl ₃	4.433±0.25	0.2187	0.9839	307.13	0.129
CCl ₄	4.685±0.28	0.2438	0.9823	275.92	0.141
C ₆ H ₆	4.100±0.18	0.1546	0.9905	525.66	0.100

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

Table 6. Correlation analysis of C_β in para-X-substituted styrenes in different solvents on using Hammett's model.

Solvent	ρ_p	S.D	r	F	f-Taft
75%EtOH	6.214±0.33	0.5045	0.9859	347.70	0.166
EtOH	6.082±0.30	0.4472	0.9884	424.01	0.154
Me ₂ SO	6.462±0.23	0.3426	0.9940	815.37	0.114
Me ₂ CO	6.266±0.21	0.3200	0.9945	878.55	0.110
CDCl ₃	5.809±0.26	0.3931	0.9899	500.55	0.145
CCl ₄	5.575±0.22	0.3365	0.9920	629.20	0.129
C ₆ H ₆	5.383±0.23	0.3453	0.9910	556.90	0.140

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

Table 7. DSP correlation analysis of C_β in meta-X-substituted styrenes in different solvents on using modified Swain-Lupton model.

Solvent	f	r	λ	S.D	R	F	f-Taft
75%EtOH	5.338±0.33	1.501±0.18	0.281	0.2005	0.9905	236.43	0.100
EtOH	5.218±0.34	1.625±0.19	0.311	0.2097	0.9899	218.82	0.109
Me ₂ SO	5.170±0.38	1.429±0.21	0.276	0.2340	0.9864	161.51	0.126
Me ₂ CO	5.250±0.36	1.500±0.20	0.286	0.2198	0.9884	191.98	0.118
CDCl ₃	4.686±0.37	1.326±0.20	0.283	0.2268	0.9844	142.97	0.134
CCl ₄	4.808±0.41	1.508±0.23	0.314	0.2535	0.9829	127.67	0.147
C ₆ H ₆	4.255±0.26	1.284±0.15	0.301	0.1611	0.9910	242.19	0.104

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

Table 8. DSP correlation analysis of C_{β} in para-X-substituted styrenes in different solvents on using modified Swain-Lupton model.

Solvent	f	r	λ	S.D	R	F	f-Taft
75%EtOH	6.194±0.87	6.222±0.48	1.005	0.5318	0.9859	156.47	0.175
EtOH	5.789±0.76	6.203±0.42	1.071	0.4668	0.9884	194.65	0.161
Me ₂ SO	6.030±0.57	6.640±0.31	1.101	0.3480	0.9945	395.56	0.115
Me ₂ CO	5.895±0.53	6.418±0.29	1.089	0.3270	0.9945	420.94	0.112
CDCl ₃	5.329±0.65	6.005±0.36	1.127	0.4003	0.9910	241.66	0.148
CCl ₄	5.238±0.57	5.713±0.31	1.091	0.3466	0.9925	296.71	0.133
C ₆ H ₆	4.735±0.55	5.647±0.30	1.193	0.3340	0.9925	298.43	0.135

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

Table 9. DSP correlation analysis of C_{β} for meta-X-substituted styrenes in different solvents on using Reynolds model.

Solvent	ρ_F	ρ_R°	λ	S.D	R	F	f-Taft
75%EtOH	4.892±0.22	2.288±0.20	0.468	0.1525	0.9945	412.20	0.076
EtOH	4.850±0.15	2.424±0.14	0.500	0.1069	0.9975	855.57	0.056
Me ₂ SO	4.868±0.17	2.059±0.15	0.423	0.1164	0.9965	665.65	0.063
Me ₂ CO	4.919±0.16	2.186±0.14	0.444	0.1105	0.9970	773.48	0.059
CDCl ₃	4.354±0.16	2.002±0.15	0.460	0.1132	0.9960	587.64	0.067
CCl ₄	4.560±0.10	2.203±0.09	0.483	0.0715	0.9985	1656.86	0.041
C ₆ H ₆	3.967±0.13	1.890±0.12	0.476	0.0886	0.9970	810.99	0.057

n=12; λ = blending constant (ρ_R°/ρ_F); R= Multiple regression coefficient; F= F-Snedecor.

Table 10. DSP correlation analysis of C_{β} for para-X-substituted styrenes in different solvents on using Reynolds model.

Solvent	ρ_F	ρ_R°	λ	S.D	R	F	f-Taft
75%EtOH	5.664±0.41	9.474±0.37	1.673	0.2820	0.9960	567.68	0.093
EtOH	5.379±0.28	9.371±0.25	1.742	0.1942	0.9980	1146.36	0.067
Me ₂ SO	5.750±0.16	9.878±0.15	1.718	0.1133	0.9995	3772.72	0.038
Me ₂ CO	5.642±0.16	9.529±0.14	1.689	0.1103	0.9995	3737.96	0.038
CDCl ₃	5.053±0.23	8.985±0.21	1.778	0.1588	0.9985	1559.05	0.059
CCl ₄	5.036±0.14	8.494±0.12	1.687	0.0939	0.9995	4096.79	0.036
C ₆ H ₆	4.476±0.22	8.439±0.20	1.886	0.1515	0.9985	1468.38	0.061

n=12; λ = blending constant (ρ_R°/ρ_F); R= Multiple regression coefficient; F= F-Snedecor.

Table 11. DSP correlation analysis of C_β for meta-X-substituted styrenes in different solvents on using Taft model.

Solvent	ρ_I	ρ_R^0	λ	S.D	R	F	f-Taft
75%EtOH	4.862±0.18	2.037±0.16	0.419	0.1264	0.9965	602.21	0.063
EtOH	4.817±0.17	2.161±0.15	0.448	0.1182	0.9970	698.36	0.061
Me ₂ SO	4.847±0.19	1.766±0.17	0.364	0.1352	0.9955	492.42	0.073
Me ₂ CO	4.899±0.20	1.883±0.18	0.384	0.1409	0.9955	473.88	0.075
CDCl ₃	4.267±0.23	1.817±0.21	0.426	0.1623	0.9920	283.24	0.096
CCl ₄	4.468±0.23	1.994±0.21	0.446	0.1662	0.9925	303.00	0.096
C ₆ H ₆	3.964±0.11	1.649±0.10	0.416	0.0794	0.9980	1010.81	0.051

n=12; λ = blending constant (ρ_R^0/ρ_I); R= Multiple regression coefficient; F= F-Snedecor.

Table 12. DSP correlation analysis of C_β for para-X-substituted styrenes in different solvents on using Taft model.

Solvent	ρ_I	ρ_R^0	λ	S.D	R	F	f-Taft
75%EtOH	5.981±0.26	8.901±0.24	1.488	0.1864	0.9985	1306.50	0.061
EtOH	5.690±0.25	8.795±0.23	1.546	0.1773	0.9985	1376.80	0.061
Me ₂ SO	6.108±0.39	9.200±0.36	1.506	0.2785	0.9965	620.14	0.092
Me ₂ CO	5.978±0.41	8.869±0.37	1.484	0.2890	0.9960	540.25	0.099
CDCl ₃	5.323±0.28	8.444±0.26	1.586	0.2018	0.9975	963.92	0.074
CCl ₄	5.272±0.26	7.972±0.24	1.512	0.1866	0.9980	1034.66	0.072
C ₆ H ₆	4.791±0.38	7.879±0.35	1.645	0.2720	0.9950	452.26	0.110

n=12; λ = blending constant (ρ_R^0/ρ_I); R= Multiple regression coefficient; F= F-Snedecor.

C_α of the meta series, gave a moderately good correlation with σ_m of Hammett model, with a reverse reaction constant in the range (-3.12)-(-4.08) (Table 13), while the para series, the correlation with σ_p , gave only crude trends in the range (-0.93)-(-1.32), but

with σ_m , gave a moderately good correlation in the range (-2.03)-(-2.72) (Table 14 and 15) respectively. This may be attributed to that, the predominate effect in C_α is the field effect.

Table 13. Correlation analysis of C_a in meta-X-substituted styrenes in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	F	f-Taft
75%EtOH	-3.438±0.25	0.2122	0.9752	196.12	0.168
EtOH	-3.472±0.26	0.2286	0.9721	172.42	0.183
Me ₂ SO	-3.312±0.28	0.2453	0.9654	163.13	0.203
Me ₂ CO	-3.413±0.33	0.2846	0.9566	107.48	0.233
CDCl ₃	-3.330±0.23	0.1974	0.9772	212.77	0.162
CCl ₄	-3.416±0.27	0.2296	0.9711	165.50	0.189
C ₆ H ₆	-4.079±0.32	0.2765	0.9706	162.59	0.191

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

Table 14. Correlation analysis of C_a in para-X-substituted styrenes in different solvents on using Hammett's model.

Solvent	ρ_p	S.D	r	F	f-Taft
75%EtOH	-1.140±0.24	0.3657	0.8307	22.26	0.325
EtOH	-1.095±0.25	0.3815	0.8087	18.88	0.337
Me ₂ SO	-1.014±0.24	0.3587	0.8044	18.30	0.335
Me ₂ CO	-1.053±0.25	0.3811	0.7975	17.49	0.349
CDCl ₃	-0.926±0.25	0.3846	0.7556	13.29	0.353
CCl ₄	-0.927±0.27	0.4020	0.7409	12.18	0.371
C ₆ H ₆	-1.322±0.28	0.4243	0.8307	22.25	0.340

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

Table 15. Correlation analysis of C_a in para-X-substituted styrenes in different solvents on using Hammett's model.

Solvent	ρ_m	S.D	r	F	f-Taft
75%EtOH	-2.371±0.17	0.1430	0.9767	205.59	0.127
EtOH	-2.293±0.19	0.1654	0.9670	143.69	0.146
Me ₂ SO	-2.128±0.19	0.1610	0.9638	130.46	0.150
Me ₂ CO	-2.215±0.21	0.1807	0.9581	112.33	0.166
CDCl ₃	-2.031±0.22	0.1901	0.9460	85.27	0.174
CCl ₄	-2.056±0.24	0.2062	0.9386	74.32	0.190
C ₆ H ₆	-2.718±0.20	0.1694	0.9752	192.23	0.136

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

C_a of the meta series, gave a moderately good correlation with a modified Swain-Lupton model, with a reverse field and resonance effects with blending constant (λ) in the range (0.32-0.36) (Table 16), while the para-series gave an excellent correlation with both solvents 75%EtOH-D₂O and CDCl₃ but all the other solvents gave a moderately correlation, with a reverse field and resonance effects with blending constant (λ) in the range(0.07-0.17) (Table 17). Reynolds and Taft models both of them gave a moderately good correlation with C_a in all solvents, for the meta-X-series, with a reverse field and resonance effects, with

blending constant (λ) in the range (0.45-0.49) and (0.39-0.43) of the Reynolds and Taft models, respectively (Table 18 and 20). While Reynolds model gave an excellent correlation in both solvents CCl₄ and C₆H₆, all the other solvents gave a moderately good correlation with blending constant (λ) in the range (0.11-0.28) (Table 19), while Taft model gave an excellent correlation with all solvent, except with both solvents CDCl₃ and Me₂SO which gave a moderately good correlation with blending constant (λ) in the range (0.07-0.21) (Table 21).

Table 16. DSP correlation analysis of C_a for meta-X-substituted styrenes in different solvents on using modified Swain-Lupton model.

Solvent	f	r	λ	S.D	R	F	f-Taft
75%EtOH	-3.499±0.36	-1.128±0.20	0.322	0.2212	0.9762	90.32	0.176
EtOH	-3.448±0.38	-1.205±0.21	0.350	0.2332	0.9742	83.10	0.186
Me ₂ SO	-3.309±0.41	-1.133±0.23	0.342	0.2541	0.9664	63.64	0.210
Me ₂ CO	-3.356±0.48	-1.208±0.26	0.360	0.2933	0.9586	50.81	0.240
CDCl ₃	-3.360±0.33	-1.116±0.18	0.332	0.2033	0.9783	100.45	0.167
CCl ₄	-3.383±0.38	-1.192±0.21	0.352	0.2359	0.9726	78.63	0.195
C ₆ H ₆	-4.027±0.46	-1.431±0.26	0.355	0.2834	0.9721	77.64	0.196

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

Table 17. DSP correlation analysis of C_a for para-X-substituted styrenes in different solvents on using modified Swain-Lupton model.

Solvent	f	r	λ	S.D	R	F	f-Taft
75%EtOH	-2.826±0.13	-0.449±0.07	0.159	0.0827	0.9930	311.17	0.074
EtOH	-2.821±0.19	-0.388±0.10	0.137	0.1147	0.9859	155.39	0.101
Me ₂ SO	-2.628±0.19	-0.352±0.10	0.134	0.1141	0.9839	135.27	0.107
Me ₂ CO	-2.742±0.26	-0.361±0.12	0.132	0.1384	0.9783	99.76	0.127
CDCl ₃	-2.680±0.17	-0.207±0.94	0.077	0.1047	0.9854	152.68	0.096
CCl ₄	-2.751±0.19	-0.179±0.11	0.065	0.1168	0.9829	126.87	0.108
C ₆ H ₆	-3.239±0.24	-0.536±0.12	0.166	0.1293	0.9869	169.07	0.104

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

Table 18. DSP correlation analysis of C_a in meta-X-substituted styrenes in different solvents on using Reynolds model.

Solvent	ρ_F	ρ_R^o	λ	S.D	R	F	f-Taft
75%EtOH	-3.398±0.21	-1.540±0.19	0.453	0.1427	0.9899	223.51	0.113
EtOH	-3.365±0.25	-1.640±0.22	0.487	0.1696	0.9864	161.12	0.135
Me ₂ SO	-3.243±0.31	-1.504±0.28	0.464	0.2136	0.9762	91.89	0.176
Me ₂ CO	-3.353±0.34	-1.575±0.30	0.470	0.2328	0.9742	83.27	0.190
CDCl ₃	-3.220±0.22	-1.563±0.20	0.485	0.1502	0.9884	187.82	0.124
CCl ₄	-3.329±0.24	-1.601±0.21	0.481	0.1624	0.9869	170.93	0.134
C ₆ H ₆	-3.957±0.30	-1.927±0.27	0.487	0.2049	0.9854	152.56	0.142

n=12; λ = blending constant (ρ_R^o/ρ_F); R= Multiple regression coefficient; F= F-Snedecor.

Table 19. DSP correlation analysis of C_a in para-X-substituted styrenes in different solvents on using Reynolds model.

Solvent	ρ_F	ρ_R^o	λ	S.D	R	F	f-Taft
75%EtOH	-2.517±0.20	-0.711±0.18	0.283	0.1361	0.9803	112.04	0.121
EtOH	-2.575±0.18	-0.556±0.16	0.216	0.1243	0.9834	131.44	0.120
Me ₂ SO	-2.360±0.21	-0.536±0.19	0.227	0.1464	0.9731	80.49	0.137
Me ₂ CO	-2.519±0.19	-0.510±0.17	0.202	0.1312	0.9803	111.53	0.120
CDCl ₃	-2.384±0.19	-0.365±0.17	0.153	0.1316	0.9772	94.99	0.121
CCl ₄	-2.498±0.15	-0.282±0.14	0.113	0.1035	0.9864	162.89	0.095
C ₆ H ₆	-2.972±0.16	-0.795±0.15	0.267	0.1123	0.9899	225.56	0.090

n=12; λ = blending constant (ρ_R^o/ρ_F); R= Multiple regression coefficient; F= F-Snedecor.

Table 20. DSP correlation analysis of C_α in meta-X-substituted styrenes in different solvents on using Taft model.

Solvent	ρ_I	ρ_R^0	λ	S.D	R	F	f-Taft
75%EtOH	-3.351±0.28	-1.330±0.26	0.397	0.1996	0.9803	111.98	0.158
EtOH	-3.331±0.31	-1.416±0.28	0.425	0.2205	0.9767	93.53	0.176
Me ₂ SO	-3.237±0.53	-1.259±0.31	0.389	0.2462	0.9685	68.06	0.203
Me ₂ CO	-3.322±0.40	-1.330±0.36	0.400	0.2819	0.9618	55.34	0.230
CDCl ₃	-3.181±0.29	-1.356±0.26	0.426	0.2043	0.9783	99.46	0.168
CCl ₄	-3.277±0.32	-1.384±0.29	0.422	0.2297	0.9742	83.14	0.189
C ₆ H ₆	-3.924±0.37	-1.649±0.34	0.420	0.2673	0.9752	87.84	0.185

n=12; λ = blending constant (ρ_R^0/ρ_I); R= Multiple regression coefficient; F= F-Snedecor.

Table 21. DSP correlation analysis of C_α in para-X-substituted styrenes in different solvents on using Taft model.

Solvent	ρ_I	ρ_R^0	λ	S.D	R	F	f-Taft
75%EtOH	-2.590±0.13	-0.506±0.12	0.195	0.0937	0.9910	246.65	0.083
EtOH	-2.579±0.13	-0.394±0.11	0.153	0.0896	0.9915	257.15	0.079
Me ₂ SO	-2.383±0.15	-0.370±0.14	0.155	0.1096	0.9849	147.10	0.102
Me ₂ CO	-2.521±0.14	-0.349±0.13	0.138	0.1022	0.9879	186.82	0.094
CDCl ₃	-2.349±0.17	-0.262±0.16	0.111	0.1225	0.9803	110.31	0.112
CCl ₄	-2.452±0.14	-0.170±0.13	0.069	0.1031	0.9864	163.97	0.095
C ₆ H ₆	-2.955±0.14	-0.624±0.12	0.211	0.0965	0.9930	307.41	0.077

n=12; λ = blending constant (ρ_R^0/ρ_I); R= Multiple regression coefficient; F= F-Snedecor.

Model performance assessment and the effect of solvent on C_α and C_β of styrene:

C_β for meta- and para-X series, for all solvents gave a moderately correlation with both models Hammett and modified Swain-Lupton. While the two models, Reynolds and Taft both of them gave an excellent correlation. C_α gave a moderately good correlation in all solvents with all models; Hammett, modified Swain-Lupton, Reynolds and Taft, for the meta series. While the Me₂SO and CDCl₃ which gave a moderately good correlation. Modified Swain-Lupton model gave an excellent

correlation in both solvents 75% EtOH-D₂O and CDCl₃, while gave a moderately good with all the other solvents. Reynolds model gave an excellent correlation with two solvents CCl₄ and C₆H₆, while gave a moderately good with all the solvents. The data of ¹³C SCS of C_α of the para series, the correlation with σ_p , gave only crude trends, while with σ_m , gave a moderately good correlation,(Table 22). This may be attributed to that, the predominate effect in C_α is the field effect.

There is no significant difference between reaction constants values in the same model, of the same atom in the same series in different solvents, as shown in the previous study(Al-Shawi, 2013). The final

conclusion, is that no solvent effect on C_α and C_β of styrene on using Hammett, modified Swain-Lupton, Reynolds and Taft models.

Table 22. A comparison of the statistical parameter f-Taft (SD/RMS) of MSP and DSP models:

Series	C atom	Solvent	Hammett	M. Swain	Reynolds	Taft		
Meta	C_β	75%EtOH	0.101	0.100	0.076	0.063		
		EtOH	0.108	0.109	0.056	0.061		
		Me ₂ SO	0.120	0.126	0.063	0.073		
		Me ₂ CO	0.111	0.118	0.059	0.075		
		CDCl ₃	0.129	0.134	0.067	0.096		
		CCl ₄	0.141	0.147	0.041	0.096		
	C_α	75%EtOH	0.168	0.176	0.113	0.158		
		EtOH	0.183	0.186	0.135	0.176		
		Me ₂ SO	0.203	0.210	0.176	0.203		
		Me ₂ CO	0.233	0.240	0.190	0.230		
		CDCl ₃	0.162	0.167	0.124	0.168		
		CCl ₄	0.189	0.195	0.134	0.189		
		C ₆ H ₆	0.191	0.196	0.142	0.185		
		Para	C_β	75%EtOH	0.166	0.175	0.093	0.061
				EtOH	0.154	0.161	0.067	0.061
				Me ₂ SO	0.114	0.115	0.038	0.092
Me ₂ CO	0.110			0.112	0.038	0.099		
CDCl ₃	0.145			0.148	0.059	0.074		
CCl ₄	0.129			0.133	0.036	0.072		
C_α	75%EtOH		0.325(0.127)	0.074	0.121	0.083		
	EtOH		0.337(0.146)	0.101	0.120	0.079		
	Me ₂ SO		0.335(0.150)	0.107	0.137	0.102		
	Me ₂ CO		0.349(0.166)	0.127	0.120	0.094		
	CDCl ₃		0.353(0.174)	0.096	0.121	0.112		
	CCl ₄		0.371(0.190)	0.108	0.095	0.095		
	C ₆ H ₆		0.340(0.136)	0.104	0.090	0.077		

M. Swain: Modified Swain-Lupton model; values between parenthesis (correlate with σ_m).

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دراسة التحليل الترابطي لتأثير المعوض باستخدام مطيافية الرنين النووي المغناطيسي C-13 .
تأثير المذيب على الازاحة الكيماوية لذرتي C_α و C_β للستايرين المعوض ميتا و بارا.

الخلاصة :

درست الإزاحات الكيماوية لمعوض الكربون-13 لذرتي الكربون (C_α , C_β) للمعوضات ميتا و بارا
ستايرين حيث: $X = H, NMe_2, OMe, Me, F, Cl, Br, CF_3, CO_2Me, COMe, CN, NO_2$
في سبعة مذيبات مختلفة ($75\%EtOH-D_2O, EtOH, Me_2SO, Me_2CO, CDCl_3, CCl_4, C_6H_6$)
درست باستخدام نوعين مختلفين من معامل المعوض: معامل المعوض أحادي الحد (MSP) (أنموذج هامت)
ومعامل المعوض ثنائي الحد (DSP) (أنموذج سواين لبتون المعدل و أنموذج رينولد و أنموذج تافت).
لا توجد اختلافات جوهرية بين قيم ثوابت التفاعل للأنموذج نفسه و للذرة نفسها و للسلسلة نفسها في مذيبات مختلفة.
فالاستنتاج النهائي لا يوجد تأثير للمذيب على C_α و C_β للستايرين باستخدام أنموذج هامت و سواين - لبتون
المعدل و رينولد و تافت.