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Effect of substituents on infrared, H^1 and C^{13} NMR spectra of 2-pyrrolyl styryl ketone

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ABSTRACT

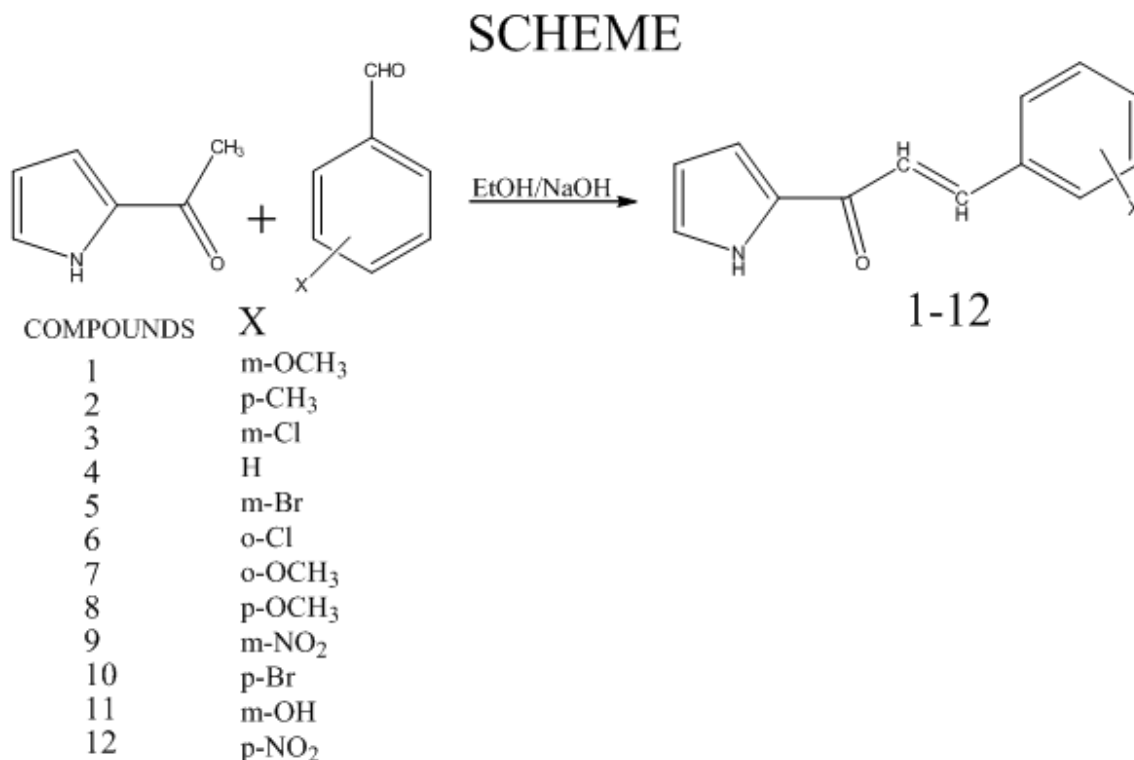
Several substituted styryl 2-pyrrolyl ketones have been prepared and their IR, H^1 and C^{13} NMR spectra are recorded. The effect of substituent on carbonyl and $>N-H$ stretching frequency was studied. The proton NMR correlated shifts (ppm) of the ethylenic and $>NH$ protons of the chalcones investigated are assigned. The correlation of C^{13} NMR chemical shifts (ppm) of C_α and C_β with Hammett substituent constants are not fair enough, σ_I and σ_R parameters also give poor correlations. Uniformly σ_I and σ_R parameters collectively explain substituent effect in few cases.

INTRODUCTION

The effect of substituents on the infrared carbonyl frequencies in several chalcones¹⁻⁵ and on C-H, C=C, CH=CH in some alkenes have been investigated. A very substantial amount of data are available on $>N-H$ stretching frequencies in heterocyclic ring systems. The proton and carbon-13 nuclear magnetic resonance spectral studies have been applied to numerous structural problems.⁶⁻¹¹ Their use in structure parameter correlations have now become very popular. A similar study involving styryl pyrrolyl ketone is utmost unknown. Hence, several *ortho*-, *meta*- and *para*-substituted 2-pyrrolyl styryl ketones were prepared and their ultraviolet, infrared, proton and carbon-13 NMR resonance spectra were recorded with a view to study the structure parameters correlations in these styryl ketones.

MATERIALS AND METHODS

The procedure of Salem A. Basaif *et al.*¹² was adopted for preparing the chalcones(1-12) under investigation (shown in scheme-1). IR spectra were recorded in KBr (pellet forms) on a Thermo Nicolet AVATAR 330 FT-IR spectrometer (ν_{max} in cm^{-1}). H^1 NMR spectra were recorded at 400 MHz on Bruker AMX 300 MHz spectrophotometer using $CDCl_3$ /DMSO as solvent and TMS (tetramethyl silane) as internal standard C^{13} NMR spectra were recorded at 125 MHz on Bruker AMX 300 MHz spectrophotometer using $CDCl_3$ as solvent



RESULTS AND DISCUSSION

IR SPECTRA

Normally chalcones show two carbonyl bands for *S*-cis and *S*-trans conformers in solution. Although an equilibrium mixture of different conformations of some of the chalcones may exist in crystalline state.

In addition to carbonyl the system under investigation also shows strong band due to the secondary amino (>N-H) group that is present in the pyrrole moiety of the system.

Effect of substituents on carbonyl and –N-H stretching frequency

The carbonyl stretching frequencies of these 2-pyrrolyl styryl ketones shows that the lowest carbonyl frequency is observed. When a powerful electron donating group is present. This may be due to the fact that electron donating group reduces the double bond character of the carbonyl band and thereby lower the frequency.

Eventhough the effectiveness are similar in *ortho* and *para* positions the increase in carbonyl absorption frequency is attributed to the loss of co-planarity of styryl group with the carbonyl group. The IR spectral values are given in Table(1)

The data which are given in the Table-1 are sperately analysed through various correlation equations involving σ and σ^+ values Fig(1-4).The results of statistical analysis are presented in Table -2

All the correlation data given in Table –2 are pertaining to single parameter equation which indicates clearly that poor correlation is obtained with Hammett σ and σ^+ constants. The single parameter correlations are shown in Figs. 1-4.

In view of the inability of some sigma constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlation involving σ_1 and σ_R constants. The correlation equations generated are shown in Table 3.

NMR SPECTRA

In general, the signals for aromatic protons present in a molecule appear in the downfield region of around 7 ppm due to magnetic anisotropic effect. In most of the cases, since the absorption of the olefinic protons in the chalcones are also in the aromatic region, it is quite difficult to differentiate the olefinic protons signal from that of the aryl protons. In such cases it is essential to go for some other techniques like INDOR double resonance. Generally of the two olefinic protons in chalcones, the one nearest to the aromatic ring (H_B proton) resonates in the deshielding region compared to that of α -proton (H_A). Because this will experience a magnetic field from the induced circulation of π electrons in the aromatic ring, which will augment the applied field and hence lead to a higher δ value.

The study of NMR chemical shifts in chalcones is well known, including this styryl ketones. Ananthakrishna Nadar and sung¹² have studied several *meta*- and *para* substituted styryl biphenyl ketones. They assigned the olefinic proton chemical shifts by using INDOR double resonance technique.

The substituent chemical shift(SCS) for the H_B proton signal is less sensitive when the substituents are in *meta*- or *para*- position. The H_B proton shift for the above mentioned substituents always lie in 7.6 to 7.9 ppm region when the substituents are present in *ortho*- position, the H_B proton signals are obtained in the downfield (8.225ppm region) compared to their *para*- counterpart (table 4)

In the cases there may be some interaction between the H_B protons and the *ortho*- substituents. In such a system there will be two opposite effects, (i) the *ortho*-substituent may push H_B proton out of the plane of the aromatic ring and this will cause less deshielding by the ring current effect, (ii) the close approach of the *ortho*- substituents and the β protons will deshield the proton. This effect arises from the distortion of the electronic cloud around H_B protons when the two atoms approach within the sum of their Van der Waals radii and can apply to H_B protons. The same trend in chemical shift value is observed irrespective of the nature of electrical effect of substituents in pyrrole ring.

The signals of the ethylene protons in all the compounds investigated in the study are assigned. The ethylenic proton signals give a doublet in most cases and are well separated from the signals of the aromatic protons H_B and the secondary amino proton present in the pyrrole ring gives only singlet (≈ 9.6 to 11.6). The chemical shifts of the protons are given in Table 4.

All the attempted correlations involving substituent parameters give only positive values for ρ . This shows that normal substituent effect is operative in all systems. This may be due to the larger inductive effect associated with 2-pyrrolyl styryl ketone. The results of statistical analysis are given in table -5

The chemical shifts observed for the protons in the present investigation for substituted 2- pyrrolyl styryl ketone do not correlate satisfactorily with substituents σ and σ^+ values.

From the table-6 It is inferred that even the correlation with σ_I and σ_R parameters also produce only a poor correlation. This can be due to the nature of the system in which the benzene ring orients itself with an angle of 180° to the plane of the molecule and also due to large distance between the protons under investigation and the substituents.

C^{13} NMR SPECTRA

The assignment of carbonyl peak in the spectra is very simple in all the cases since it appears as a clear single peak in the region of 177.14-179.0 (ppm). The most striking feature of carbonyl carbon resonance position for these chalcone is apparent due to lack of sensitivity towards the variety of substituents.

The presence of *ortho* - substituents in these chalcones show small changes in the C_a chemical shifts, but no pronounced variations are found for compounds with *ortho*-substituents compared to their *para*-counterpart. In the cases of C_b carbons, there are appreciable changes in the chemical shifts. when *ortho*- substituents are present in the styryl part compared with their *para* counterpart. The pronounced difference in chemical shifts ($\Delta\delta \approx 3-4$ ppm) may be due to the steric interference to co-planarity of the styryl part. The difference in chemical shifts for carbons is very ($\Delta\delta \approx 1-2$ ppm) low.

The correlations of carbonyl chemical shifts with σ constants gives poor correlation ($r=0.743$; $n=12$). This is attributed to the lack of sensitivity of the carbonyl group to the substituent effect.

The C^{13} chemical shifts values of C_α and C_β carbons of substituted styryl pyrrolyl ketones are correlated with various Hammett substituent constants. The results of statistical analysis of substituent effect of C_α and C_β carbons are shown in Table 7. Since the correlations with Hammett substituent constants are very poor it was thought worthwhile to seek multiple correlations involving σ_I and σ_R constants. The correlations equations generated are shown in Table 8. The single parameter correlations are shown in Figs.5-6. But the correlations with σ^+ values is slightly better.

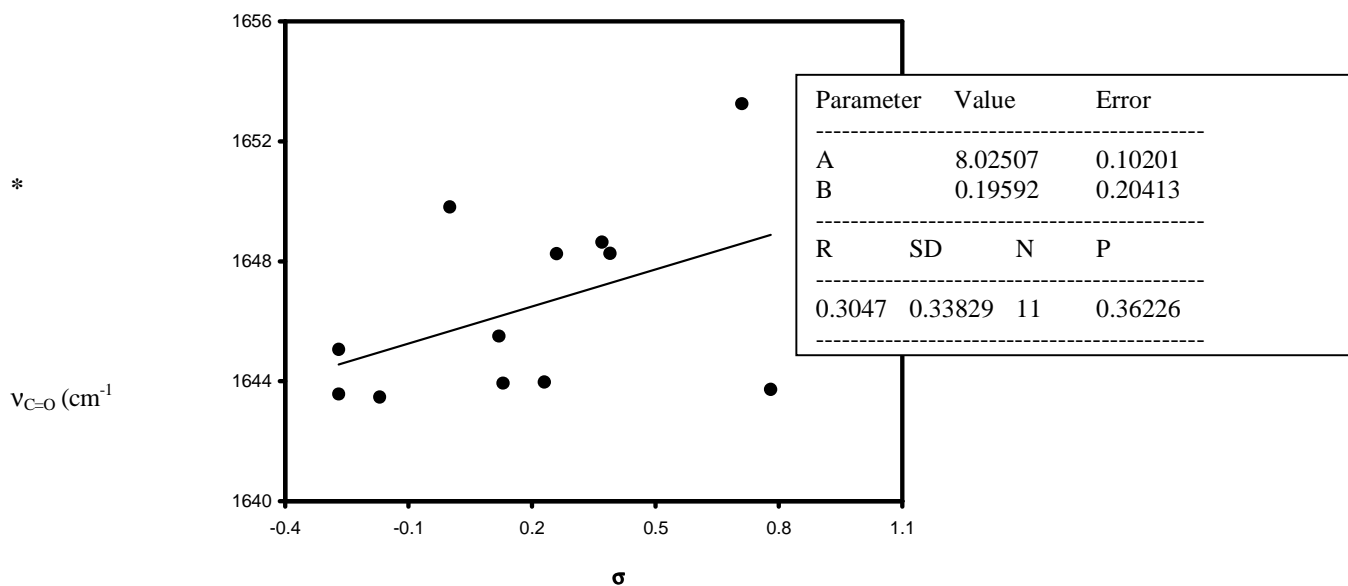


Fig 1 Plot of $\nu_{C=O}$ (cm^{-1}) substituted 2-pyrrolyl styryl ketone versus σ

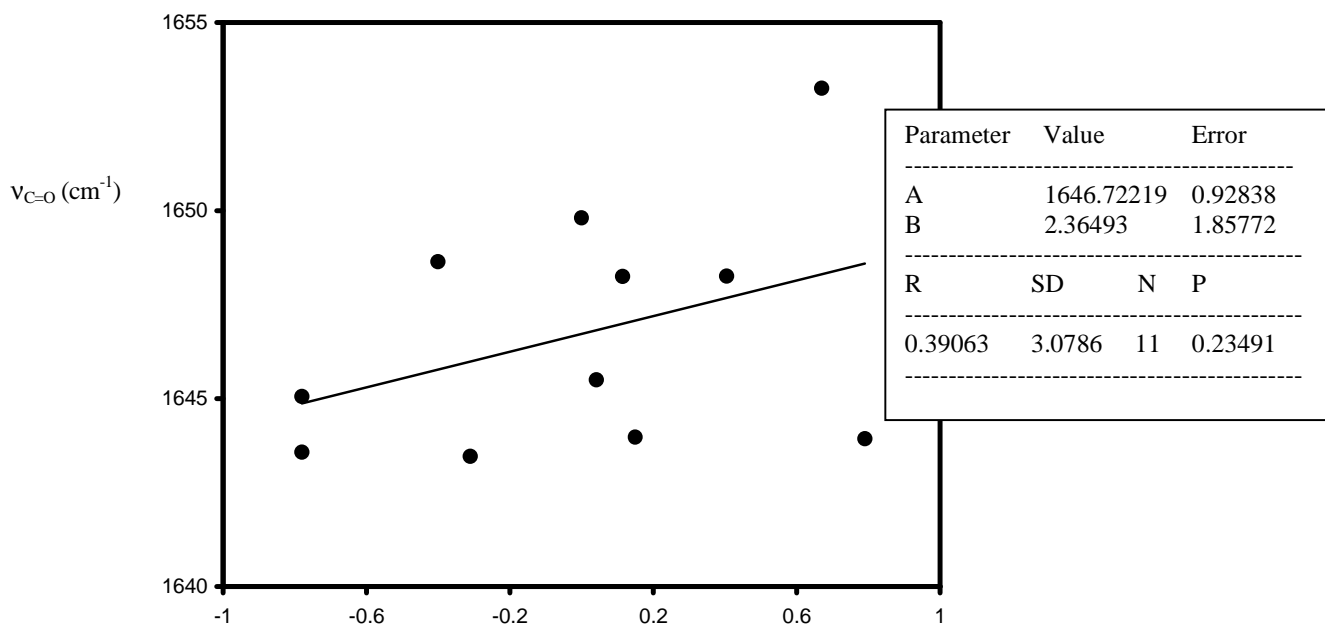


Fig 2. Plot of $\nu_{C=O}$ (cm^{-1}) substituted 2-pyrrolyl styryl ketone versus σ^+

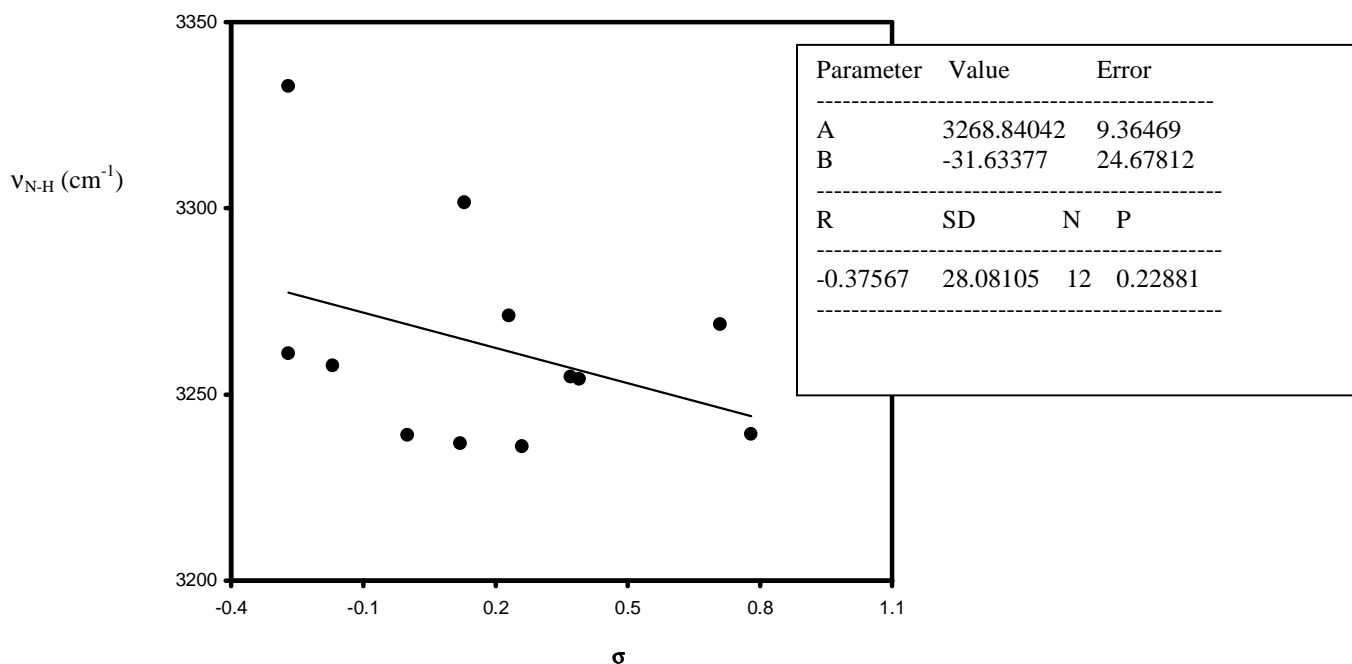


Fig.3. Plot of ν_{N-H} (cm^{-1}) of substituted 2-pyrrolyl styryl ketone versus σ

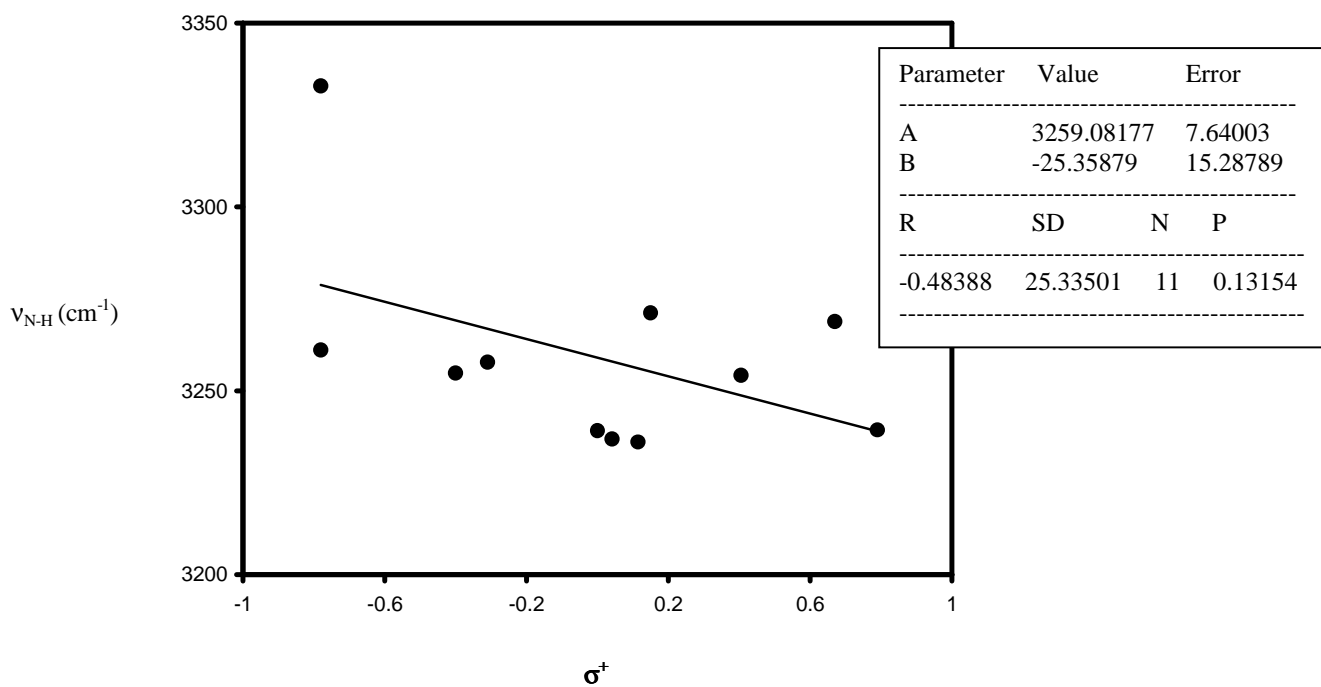


Fig.4. Plot of ν_{N-H} (cm^{-1}) of substituted 2-pyrrolyl styryl ketone versus σ^+

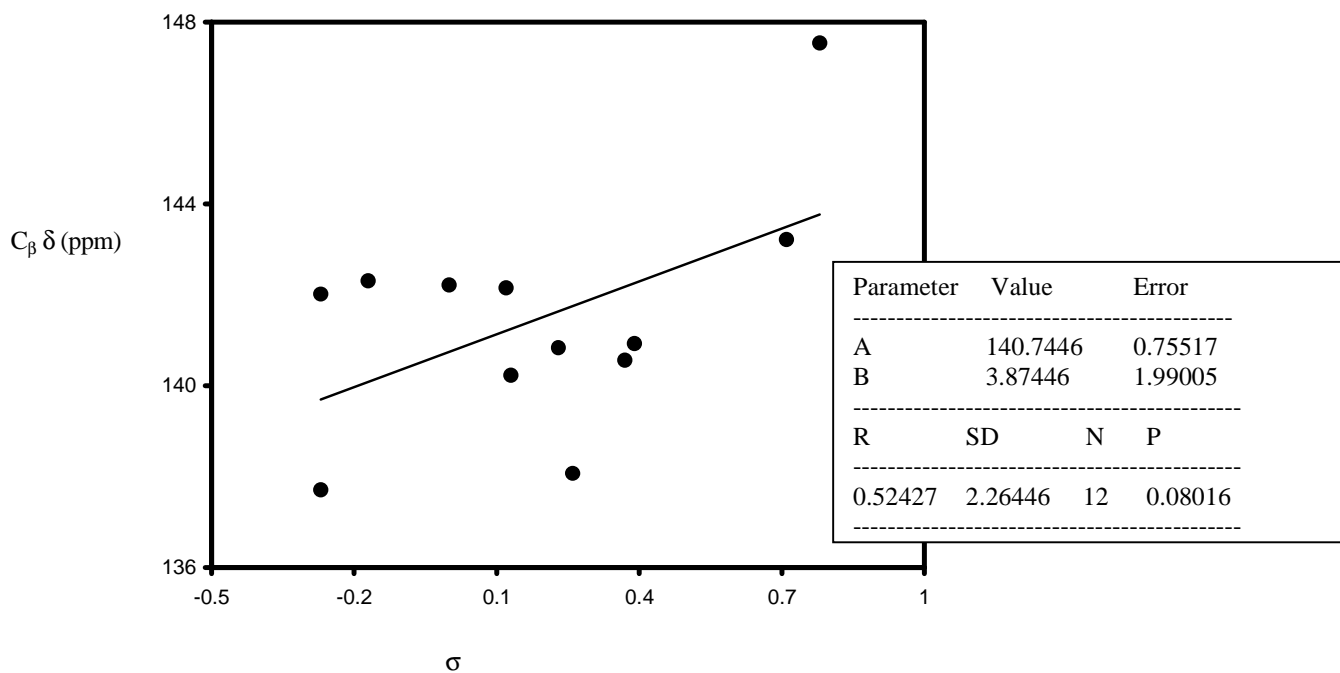


Fig.5. Plot of $C_{\beta} \delta$ (ppm) of substituted 2-pyrrolyl styryl ketone versus σ

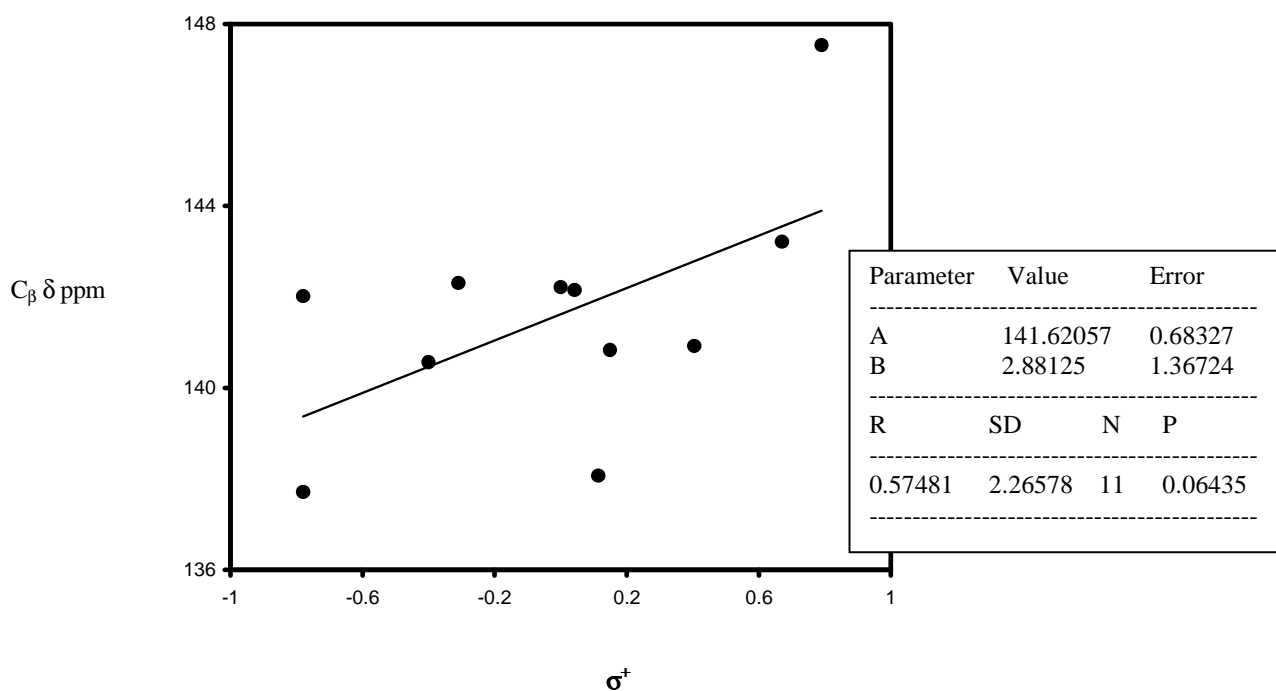


Fig.6. Plot of $C_{\beta} \delta$ (ppm) of substituted 2-pyrrolyl styryl ketone versus σ^+

Table-1 Carbonyl and >N-H stretching frequencies of substituted 2-pyrrolyl styryl ketone

No.	Substituents	$\nu_{C=O}$ (cm ⁻¹)	$\nu_{>N-H}$ (cm ⁻¹)
1.	<i>m</i> -OCH ₃	1645.50	3236.90
2.	<i>p</i> -CH ₃	1643.47	3257.77
3.	<i>m</i> -Cl	1648.64	3259.81
4.	H	1649.81	3239.14
5.	<i>m</i> -Br	1648.26	3254.19
6.	<i>o</i> -Cl	1648.25	3236.12
7.	<i>o</i> -OCH ₃	1645.06	3261.03
8.	<i>p</i> -OCH ₃	1643.57	3332.89
9.	<i>m</i> -NO ₂	1653.25	3268.90
10.	<i>p</i> -Br	1643.97	3271.23
11.	<i>m</i> -OH	1643.93	3301.58
12.	<i>p</i> -NO ₂	1643.73	3239.40

Table-2 Results of statistical analysis of carbonyl and >N-H stretching frequencies of 2-pyrrolyl styryl ketone

System	Constant for correlation	A	B	S.D	R	Substituent
$\nu_{X=O}$ (v μ)	σ	1645.5	4.4017	2.9463	0.464	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH
	σ^+	1646.6	2.340	3.0786	0.381	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl
$\nu_{>N-H}$ (v μ)	σ	3269.1	-30.95	28.080	0.370	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH
	σ^+	3259.5	-26.06	25.35	0.498	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl

Table-3 Correlation equation with σ_I and σ_R constants

System	Correlation equation in $\nu_{C=O}$ (cm ⁻¹)	Substituent
2-Pyrrolyl styryl ketone	$\nu_{X=O} = 1646.96 + 5.6906 \sigma_I + 6.5964 \sigma_P$ (P = 0.743, $\Sigma\Delta = 2.255$, $\nu = 12$)	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH
	$\nu_{>N-H} = 3246.62 + 4.4813 \sigma_I - 53.4705 \sigma_P$ (P = 0.492, $\Sigma\Delta = 28.14$, $\nu = 12$)	

Table.4 H¹ NMR chemical shifts of protons in Substituted styryl pyrolyl ketone

No	Substituent	δ (ppm) -CH=CH-	δ (ppm) >N-H
1.	<i>m</i> -OCH ₃	7.801	10.005
2.	<i>p</i> -CH ₃	7.889	10.047
3.	<i>m</i> -Cl	7.749	9.767
4.	H	7.847	10.352
5.	<i>m</i> -Br	7.788	9.872
6.	<i>o</i> -Cl	8.225	10.180
7.	<i>o</i> -OCH ₃	7.788	10.230
8.	<i>p</i> -OCH ₃	8.128	10.258
9.	<i>m</i> -NO ₂	8.241	9.589
10.	<i>p</i> -Br	7.756	10.062
11.	<i>m</i> -OH	7.643	11.661
12.	<i>p</i> -NO ₂	8.360	11.691

Table-5 Results of statistical analysis of chemical shift of protons of substituted 2-pyrrolyl styryl ketone

Systems	Constants for correlation	r	I	ρ	S	n	Substituents
2-Pyrrolyl styryl ketone	$\sigma\delta$ -CH=CH-	0.423	7.872	0.298	0.3284	12	<i>m</i> -OCH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -Cl, H, <i>m</i> -Br, <i>m</i> -OH, <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -NO ₂ , <i>p</i> -Br, <i>p</i> -NO ₂
	$\sigma+\delta$ -CH=CH-	0.448	7.963	0.196	0.3384	11	<i>m</i> -OCH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -Cl, H, <i>m</i> -Br, <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -NO ₂ , <i>p</i> -Br, <i>p</i> -NO ₂
	δ >N-H	0.127	10.26	0.249	0.5568	12	<i>m</i> -OCH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -Cl, H, <i>m</i> -Br, <i>m</i> -OH, <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -OCH ₃ , <i>m</i> -NO ₂ , <i>p</i> -Br, <i>p</i> -NO ₂

Table-6

System	Correlation equation	Substituent
2-Pyrrolyl styryl ketone	δ_H (ppm) = 7.908 + 0.428119 σ_I -CH=CH- + 0.3986 σ_R R = 0.0855; SD = 0.7418; n = 12	<i>m</i> -OCH ₃ , <i>p</i> -CH ₃ , <i>m</i> -Cl, H, <i>m</i> -Br, <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -OCH ₃ , <i>p</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -OH, <i>p</i> -NO ₂
	δ_H (ppm) = 10.277 - 0.089 σ_I - >N-H 0.1966 σ_R R = 0.631; SD = 0.203; n = 12	<i>m</i> -OCH ₃ , <i>p</i> -CH ₃ , <i>m</i> -Cl, H, <i>m</i> -Br, <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -OCH ₃ , <i>p</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -OH, <i>p</i> -NO ₂

Table 7. Results of statistical analysis of chemical shifts of C_α and C_β carbons of substituted styryl pyrrolyl ketones

Systems	Types of carbon	Constants for correlation	r	I	ρ	S	N	Substituent
2-Pyrrolyl styryl ketone	C _α	σ	0.1627	121.21	0.872	1.9018	12	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH
		σ ⁺	0.0577	121.42	0.219	2.2645	11	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl
	C _β	σ	0.5242	140.74	3.870	2.0303	12	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH
		σ ⁺	0.5748	141.62	2.880	2.2658	11	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl

Table 8. Results of statistical analysis of chemical shifts of C_α and C_β carbons of substituted styryl pyrrolyl ketones

System	Correlation equation in		Substituent
	δ C _α (ppm) carbon	δ C _β (ppm) carbon	
2-pyrrolyl Styryl ketone	δ C _α (ppm) = 121.504+0.8192 δ _I +1.2708 δ _R R = 0.217; SD = 1.983; n = 12	δ C _β (ppm) = 142.78+1.3841 δ _I + 5.438 δ _R R = 0.5946; SD = 2.25; n = 12	X = H, <i>m</i> -OCH ₃ , <i>p</i> -NO ₂ , <i>p</i> -OCH ₃ , <i>o</i> -Cl, <i>o</i> -CH ₃ , <i>p</i> -CH ₃ , <i>p</i> -Br, <i>m</i> -Br, <i>m</i> -NO ₂ , <i>m</i> -Cl, <i>m</i> -OH

CONCLUSION

When correlations were made for carbonyl and >N-H stretching frequencies with σ and σ⁺ constants only a fair correlation was obtained. The proton NMR correlated shifts (ppm) of the ethylenic and >N-H protons of the chalcones investigated are assigned. Their correlations involving various substituent parameters give positive ρ values. The correlation of C¹³ NMR chemical shifts (ppm) of C_α and C_β with Hammett substituents constants. σ_I and σ_R parameters collectively explain substituents effect in some cases.

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