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QSPR STUDY IN SUBSTITUTED STYRYL 9H–FLUORENYL AND BIPHENYL KETONES FROM IR SPECTRA

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ABSTRACT

Two series of chalcones (9H–fluorenyl and biphenyl ketones) were synthesized by microwave oven irradiation process. Their infrared spectra (KBr, 400–4000 cm^{-1}) were recorded and the carbonyl stretching frequencies of *s–cis* and *s–trans* conformers were assigned. These data were correlated with Hammett's substituent constants. The results of statistical analysis QSPR study in the above ketones has been discussed. It failed in 9H–fluorenyl ketones but biphenyl ketones were brightly explained the QSPR with methylene resonance.

Key words: Chalcones, IR spectra, QSPR study

INTRODUCTION

In 1970's, the correlation study involved the prediction of ground state molecular equilibrations[1,2] such as *s–cis* and *s–trans* isomers of alkenes, alkynes, benzoyl chlorides, styrenes and α, β–unsaturated ketones. The stepwise growth of correlation study is to enter into the transition state study of reaction mechanism[3], biological activities[4] and normal coordinate analysis[5,6], etc. f organic compounds. Now a days scientists[7,8] have paid more interest to correlate the group frequencies of spectral data with Hammett's substituent constants to explain the QSAR, QPR and QSPR study of the organic substrates. With in the above view, there is no information available in literature in the past. So two series of substituted styryl 9H–fluorenyl and biphenyl ketones were synthesized and the QSPR study of the compounds from infrared spectra was made.

EXPERIMENTAL

A mixture of various *m* – and *p* – substituted benzaldehydes (0.01mol) with 2–acetyl 9H–fluorene and 4–acetyl biphenyl (0.01 mol) and zinc chloride (0.001 mol) was taken in ACE tube, flushed with oxygen and tightly capped. These mixtures are subjected to microwave oven heating for 5–7 minutes in a domestic oven (KENSTAR–Wave Reflection System, 900 Watts, and DMO) and then it is allowed to reach room temperature. The separated solid was filtered, dried and crystallized with ethanol to constant melting point [9, 10]

Infrared spectra of above chalcones were recorded in Perkin Elmer FT IR (KBr, 400–4000 cm^{-1}) in Department of Biotechnology, St. Peter Engineering College, Avadi, Chennai.

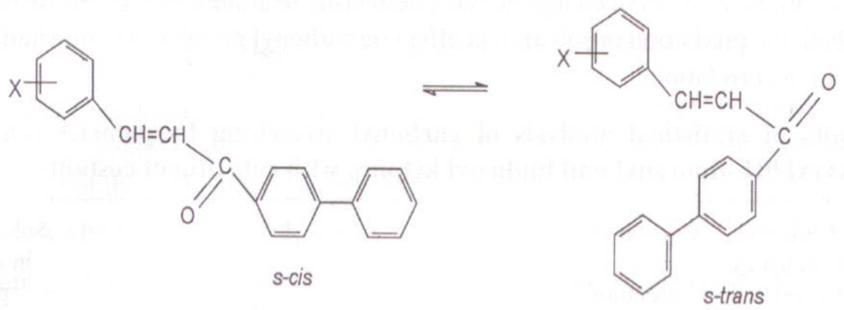
RESULTS AND DISCUSSION

The compounds chosen for present investigation are a,β–unsaturated ketones. These can exist in *s–cis* and *s–trans* conformers (I and II). Structure (I) and (II) are same but differ with $-CH_2-$group. The infrared spectra were all recorded on the KBr disk in order to avoid the shoulder formation[11, 12] on carbonyl doublets. The s–cis conformers exhibit higher frequencies for carbonyl absorption compared to those exhibited by s–trans conformers. The stretching frequencies for carbonyl absorptions are assigned based on the assignments made by Hays and Timmons[13]. These are tabulated in Table 1, and were separately analyzed through various correlation equations. The results of statistical analysis[14] are presented in Table 2.

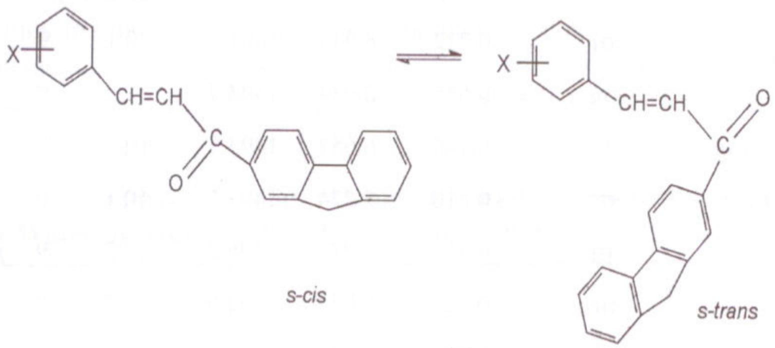
Table 1. *s–cis* and *s–trans* carbonyl stretching frequencies (cm^{-1}) of substituded styryl 9H–fluorenyl and biphenyl ketones

Substituents	9H–Fluorenyl ketones		Biphenyl ketones	
	s–cis	*s–trans*	*s–cis*	*s–trans*
H	1597	1476	1698	1670
m–NH_2	1598	1526	1694	1664
m–Cl	1590	1561	1699	1677
p–Cl	1596	1522	1699	1672
p–$N(CH_3)_2$	1597	1524	1692	1668
p–OH	1622	1545	1688	1673
p–OCH_3	1597	1545	1693	1670
m–NO_2	1596	1575	1703	1680
p–NO_2	1594	1575	1705	1684

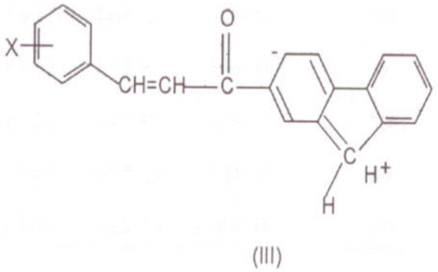
The analysis of the data in (Table–2) reveals that the substituent effect has a good correlation with Hammett σ constants in biphenyl system. On the other hand all the correlation failed (with negative correlations) in 9H–fluorenyl system. A comparison of values for two isomers in relation to σ constants indicates that their relative abilities to transmit electronic effects are very similar. The ratio of ρ_{cis}/ρ_{trans} is 0.99. This results is in accordance with the hypothesis that as the two conformers approach simple degree of coplanarity and C–C free



(I)



(II)



(III)

Where X= H, *m*-NH_2, *m*-Cl, *p*-Cl, *p*-$N(CH_3)_2$, *p*-OH, *p*-OCH_3, *m*-NO_2, *p*-NO_2

rotation; it assist to predict the correlation coefficient in biphenyl system. But there is no coplanarity and C–C free rotation in 9H–fluorenyl system and $-CH_2-$ group resonates with the fluorene ring and produce negative charge on one phenyl ring near the carbonyl group (III) and is highly disturbed, the prediction of substituent effect on carbonyl group absorption and hence, it produces negative correlation.

Table 2. Results of statistical analysis of carbonyl stretching frequencies (cm^{-1}) of substituded styryl 9H–fluorenyl and biphenyl ketones with substituent costants

System	Carbonyl Frequency Correlated	Constants for Correlation	r	ρ	I	s	n	Substituent in styryl part
9H–fluorenyl ketones	*s–cis*	σ	– 0.623	– 8.302	1599.2	26.6	9	
		σ^+	– 0.445	– 5.925	1597.9	20.1	9	
		σ_I	– 0.722	– 8.949	1601.3	30.1	9	H
		σ_R	– 0.648	– 0.034	1598.7	31.8	9	*m*–NH_2
	s–trans	σ	– 0.408	– 6.657	1493.7	10.3	9	*m*–Cl
		σ^+	– 0.510	– 5.274	1494.2	10.1	9	*p*–Cl
		σ_I	– 0.356	– 5.937	1496.2	12.2	9	*p*–$N(CH_3)_2$
		σ_R	– 0.422	– 0.033	1494.9	11.7	9	*p*–OH
Biphenyl ketones	*s–cis*	σ	0.983	8.310	1693.2	1.25	9	*p*–OCH_3
		σ^+	0.943	10.212	1694.5	1.78	9	*m*–NO_2
		σ_I	0.922	11.348	1695.3	1.98	9	*p*–NO_2
		σ_R	0.901	12.504	1693.5	2.03	9	
	s–trans	σ	0.943	8.223	1675.8	1.03	9	
		σ^+	0.946	9.216	1674.3	1.22	9	
		σ_I	0.912	12.520	1657.8	1.68	9	
		σ_R	0.900	11.220	1676.3	2.31	9	

Similarly the multiple correlations involving either s_I or s_R constants or Swain–Lupton[15] constants, F & R parameters produced good correlations in biphenyl ketones and failure in fluorenyl system. The correlation equations regenerated are shown in Table 3. This is due to the fact that the methylene resonance highly disturbs the effect of substituent on carbonyl stretching in fluorenyl ketones.

Table 3. Results of statistical analysis of carbonyl stretching frequencies (cm^{-1}) of substituted styryl 9H–fluorenyl and biphenyl ketones with σ_I, σ_R or F and R parameters

System	Confor-mers	Correlation equation for σ_I, σ_R	Correlation equation for F & R	Substi-tuents
Biphenyl ketones	*s–cis*	$\nu_{C=O}$ = 1635.3+7.62 σ_I+5.43 σ_R (±0.25) (±0.35) (±0.71) (R = 0.999, n = 9, P>99%)	$\nu_{C=O}$ = 1628.3 + 4.03F + 6.72R (±0.71) (±0.21) (±0.85) (R = 0.999, n = 9, P>99%)	H *m*–NH_2 *m*–Cl *p*–Cl p–$N(CH_3)_2$ *p*–OH *p*–OCH_3 *m*–NO_2 *p*–NO_2
	s–trans	$\nu_{C=O}$ = 1655.2+6.32 σ_I+3.03 σ_R (±0.35) (±1.01) (±0.71) (R = 0.999, n = 9, P>99%)	$\nu_{C=O}$ = 1644.3 + 5.10F + 3.12R (±0.22) (±7.28) (±0.65) (R = 0.999, n = 9, P>99%)	
9H–fluorenyl ketones	*s–cis*	$\nu_{C=O}$ = 1588.8–4.32 σ_I+0.01 σ_R (±1.02) (±11.32) (±5.72) (R = 0.722, n = 9, P>60%)	$\nu_{C=O}$ = 1603.5 + 8.02F + 1.13R (±2.23) (±8.37) (±5.32) (R = 0.80, n = 9, P>65%)	
	s–trans	$\nu_{C=O}$ = 1483.7–3.21 σ_I+1.17 σ_R (±1.17) (±11.33) (±22.1) (R = 0.557, n = 9, P<60%)	$\nu_{C=O}$ = 1414.3 + 9.17F + 0.13R (±1.11) (±8.03) (±2.31) (R = 0.810, n = 9, P>75%)	

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