Substituent Effect on the Infrared Spectra of Thiazolyl Styryl Ketone

R. Rajalakshmi [a*], S. Ramkumar [a] and R. Arulmani [a]

[a] *Department of Chemistry, Annamalai University, Annamal Ainagar - 608002,Tamil Nadu, India.*

Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

A series of *p*-substituted thiazolyl styryl ketones were synthesized by the Claisen -Schmidt condensation of various substituted benzaldehydes with 5-acetyl-2,4-dimethyl thiazole. The IR spectra for all the chalcones were recorded and effect of substituent on the carbonyl and C=N stretching frequencies are analyzed.

Keywords: Thiazolyl styryl ketones; chalcones; IR spectra; stretching frequency.

1. INTRODUCTION

The infrared spectra of $\alpha,\beta-$unsaturated ketones throw light on the conformations of such molecules [1-3]. Normally the carbonyl stretching frequencies in infrared spectra of carbonyl compounds appear at 1850-1650 cm^{-1}. The frequency of carbonyl absorption is almost entirely determined by the nature of its immediate surroundings, and the architecture of the rest of the molecule is of little importance unless it is such that it causes chelation (or)

some similar effect. Thus the carbonyl frequency shifts away from the normal position in $\alpha,\beta-$unsaturated materials and toward carbonyl compounds with strongly electronegative substituents on the $\alpha-$carbon atom whilst in cyclic ketones the frequency shift and its direction are related to the degree of strain of the ring [4-23]. The frequency wave number decreases with the increasing electron withdrawing tendency of the group. The force constant of C=O is evaluated by the distribution of electron density around the linkage [20-21].

Corresponding author: Email: chemrajalaksmi@gmail.com;

Several investigations have shown that the infrared wave number shifts of "mass insensitive" stretches can be correlated with inductive and mesomeric effects [14,17] and other important physical properties [21-24]. Polar effects have a large influence on infrared frequencies and are largely independent of mass (or) combination effects. The substituent's inductive and mesomeric effects have an impact on the stretching frequency wave number .Hence the present investigation focused on the substituent effect on the infrared frequency of carbonyl group in the thiazoly lstyryl ketone.

2. EXPRIMENTAL

2.1 Preparation of Chalcones

The ethanolic solution of 5-acetyl-2,4-dimethyl thiazole (0.4049g) and 4-methylbenzaldehyde (0.3537g) is refluxed with small quantity of 10 N sodium hydroxide solution for 40 hrs. The resulting solution is poured into ice-water and the formed precipitate is filtered. The crude chalcone is recrystallized from ethanol.

2.2 IR Measurement

IR spectrum was recorded on AVATAR-NICOLET 330 FT-IR spectrophotometer. The sample was mixed with KBr and the pellet technique was adopted to record the spectrum. The IR spectrum were recorded for liquid samples using liquid cells.

3. RESULTS AND DISCUSSION

The compounds chosen for the study are substituted thiazolyl styryl ketone in the present investigation. The infrared spectra of all the compounds are recorded in KBr disc. A number of investigations have been previously reported on the

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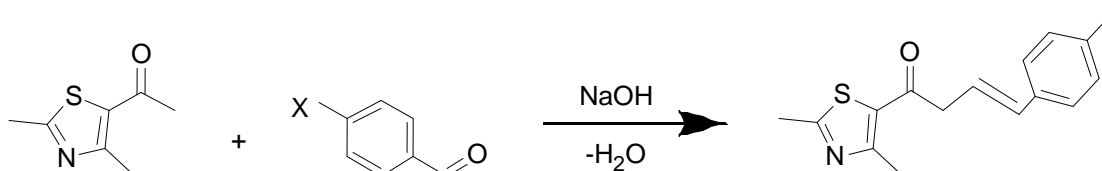
where X is

1-H
2.-Cl
3-Br
4-OCH$_3$
5-NO$_2$
6-CH$_3$

Table 1. Physical constants of styryl thiazolyl ketone

Compound	Molecular formula	Molecular weight	Melting point (^{0}C)
1	$C_{14}H_{12}ONS$	242.35	152.2
2	$C_{14}H_{12}ONS\ Cl$	282.36	165.2
3	$C_{14}H_{12}ONSBr$	321.02	173.3
4	$C_{15}H_{15}O_2NS$	273.05	158.7
5	$C_{14}H_{12}O_3N_2S$	315.00	170.5
6	$C_{15}H_{15}ONS$	257.35	162.2

effect of substituents on the infrared carbonyl frequencies of various systems [24-25]. In solution, chalcones usually have two carbonyl bands for s-cis and s-trans conformers. In solution, an equilibrium combination of various conformations of some of the chalcones may exist, but in the crystalline state, only one form is expected to exist. This hypothesis has been well supported by the spectral data obtained by earlier workers [25,26]. The stretching frequencies of carbonyl absorptions are assigned based on the assignments made by earlier workers [27,28].

In addition to the carbonyl absorption, the system under investigation also shows a strong band due to (>C=N) group [Fig.1].

Azoles have been studied by Fuson and Josien and Jones and Moritz [29]. They found an overall range of 1598 to 1625 cm^{-1} and the latter authors have developed an equation which allows the calculation of the frequency in thiazoles variously substituted with methyl or carbethoxy groups in different positions. Marion et al. [30] quote a range of 1620-1640 cm^{-1} for related systems in alkaloids.

A very substantial amount of data is available on >C=N stretching frequencies in heterocyclic ring systems. Indoles have been studied by Fuson et al. [30], Witkopand Marion and Vampiri [31-34]. Indole itself absorbs at1625cm^{-1} but values as low as 1601 cm^{-1} are quoted for some derivatives. However, because not all examples were evaluated in dilute solution, it's unlikely that this is entirely due to substituent effects, and it's more likely that self association is to blame for much of the shift.

3.1 Effect of Substituent on Carbonyl and >C=N Stretching Frequency

The carbonyl stretching frequencies of these thiazolyl styryl ketones show that the lowest carbonyl frequency is observed when a powerful electron donating group is present. This may be due to the fact that an electron donating group reduces the double bond character of the C=O bond and thereby lower the frequency. Even though the effectiveness of substituents are similar in *ortho*- and *para*-positions, the increase in C=O absorption frequency is attributed to the loss of co-planarity of the styryl group with the carbonyl group. The IR spectral values are furnished in Table 2. Infrared spectrum of *p*-methyl substituted styryl thiazolyl ketone is shown in Fig.1.

The carbonyl and >C=N stretching vibrations are given in Table 2. The data are separately analyzed through various correlation equations involving σ and σ^+ values. The results of the statistical analysis are presented in Table 3.

Table 2 shows that all of the correlation data is for a single parameter equation, indicating that Hammett σ and σ^+ constants produce low correlation.

Table 2 shows the single parameter correlations. In view of the inability of some sigma constants to produce individually satisfactory correlations, it was thought worthwhile to seek multiple correlations involving σ_I and σ_R constants. Table 4 shows the correlation equations that were produced.
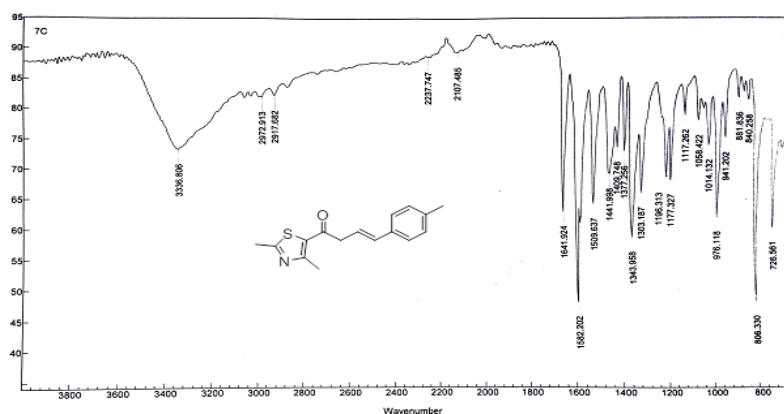

Fig.1. IR spectrum of thiazolyl styryl ketone

Table 2. Carbonyl and >C=N stretching frequencies of substituted thiazoly styryl ketone

S. No.	Substituents	$\nu_{C=O}$ (cm^{-1})	$\nu_{>C=N}$(cm^{-1})
1.	H	1666.47	1597.22
2	*p*-CH$_3$	1682.81	1582.14
3.	*p*-OCH$_3$	1677.57	1577.22
4	*p*-Br	1687.97	1599.72
5.	*p*-Cl	1683.93	1598.12
6	*p*-NO$_2$	1693.73	1607.22

Table 3. Results of statistical analysis of carbonyl and >C=N stretching frequencies of thiazolyl styryl ketone

System	Constant for correlation	A	B	S.D	R	Substituent
$\nu_{C=O}$ (nm)	σ	1675.5	4.4017	2.9463	0.464	X = H, *p*-NO$_2$, *p*-OCH$_3$, *p*-CH$_3$, *p*-Br,*p*-Cl
	σ^+	1646.6	2.340	3.0786	0.381	X = H, *p*-NO$_2$, *p*-OCH$_3$, *p*-CH$_3$, *p*-Br, *p* -Cl
$\nu_{>C=C<}$ (nm)	σ	1621.1	-30.95	28.080	0.370	X = H, *p*-NO$_2$, *p*-OCH$_3$, *p*-CH$_3$, *p*-Br, *p* -Cl
	σ^+	1617.5	-26.06	25.35	0.498	X = H, *p*-NO$_2$, *p*-OCH$_3$, *p*-CH$_3$, *p*-Br,*p* -Cl

A = Intercept; B = Slope

Table 4. Correlation equation with σ_I and σ_R constants

System	Correlation equation in $\nu_{C=O}$ (cm^{-1})	Substituent
Thiazolyl styryl ketone	$\nu_{C=O}$ = 1686.96 + 5.6906 σ_I + 6.5964 σ_R (R = 0.843, S.D = 2.255, n = 6) $\nu_{>.c=n}$ = 1589.62 – 4.4813 σ_I – 53.4705 σ_R (R = 0.792, S.D = 27.14, n = 6)	X = H, *p*-NO$_2$, *p*-OCH$_3$, *p*-CH$_3$, *p*-Br, *p* -Cl

From the above table that the multiple correlation involving σ_I and σ_R constants it is observed there is a slight improvement in the R value compared with the single parameter correlation.

4. CONCLUSION

Several *para* substituted styryl thiazolyl ketones were prepared and their infrared spectra were recorded. When correlations were made for carbonyl and >C=N stretching frequencies with σ and σ^+ constants only a fair correlation was obtained.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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