

## Substituent Effects on Carbonyl Stretching Frequencies in Substituted Styryl-2-Naphthyl Ketones

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Some substituted styryl-2-naphthyl ketones were prepared and their carbonyl stretching frequencies ( $\text{cm}^{-1}$ ) were recorded and assigned from IR (KBr, 4000–400  $\text{cm}^{-1}$ ) spectra. These data are correlated with Hammett parameter using single and multi-correlations with F and R functions. From the statistical analysis results the substituent effects on carbonyl group are predicted.

**Key Words:** Substituent effects, Carbonyl frequencies, Styryl-2-naphthyl Ketones

### INTRODUCTION

There is considerable information in literature concerning transmission of electronic effects in molecules undergoing isomer equilibration in ground state. For example,  $\alpha,\beta$ -unsaturated ketones exist as *s-cis* and *s-trans* isomers which are confirmed by infrared spectroscopy<sup>1</sup>. Mulliken<sup>2</sup> investigates the physico-chemical properties of the above system including those of polyenes and he observed equilibrium mixtures of almost planar conformers. Several investigations have shown that the infrared wavenumber shifts of “mass insensitive” stretches can be correlated with inductive and mesomeric effects<sup>3,4</sup> and other important physical properties<sup>5–7</sup> including empirical correlation<sup>8</sup>. Similar study in substituted styryl-2-naphthyl ketones is not available in literature. Hence the authors have prepared some substituted styryl 2-naphthyl ketones and recorded their infrared spectra with KBr disk with a view to seek structure-parameter correlations in these ketones.

### EXPERIMENTAL

Substituted styryl-2-naphthyl ketones were synthesized by literature method<sup>9,10</sup>. Treating a mixture of appropriate amount of benzaldehydes (0.01 mol) in ethanol (50 mL) with 2-acetylnaphthalene (0.01 mol) in presence of 10% sodium hydroxide solution (5 mL). All the compounds were recrystallised from ethanol to constant m.p.<sup>11–14</sup>.

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Infrared spectra of compounds were recorded using JASCO-700 spectrometer, (4000–400  $\text{cm}^{-1}$ ) range at the Department of Chemistry, Annamalai University, Annamalai-Nagar, (T.N.).

## RESULTS AND DISCUSSION

The compounds chosen for investigation in the present study are  $\alpha,\beta$ -unsaturated ketones. They can exist in *s-cis* and *s-trans* conformations (Fig. 1).

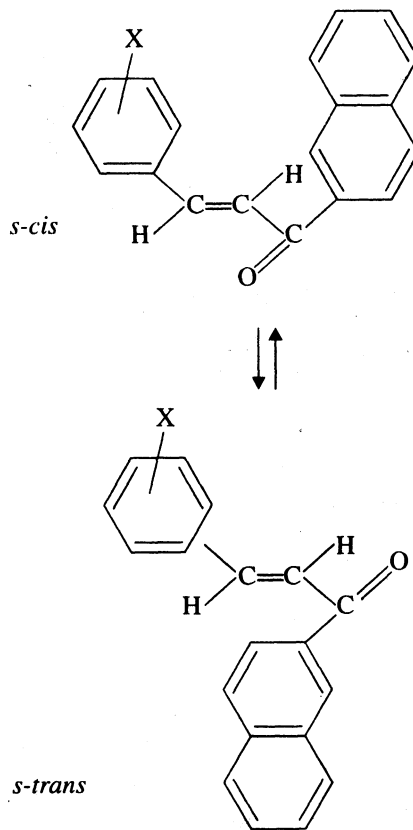


Fig. 1. X =  $m^-$  or  $p^-$  substituent

The infrared spectra were all run on KBr disk. They were all recorded on the disk in order to avoid the possibility of one of the conformers in solution<sup>15, 16</sup> exhibiting a very intense band for that conformer, thereby suppressing the existence of the other conformer producing only shoulders. The formation of less intense shoulders in solution might, in many cases, escape our attention. These complications are avoided in the present work by recording IR spectra on KBr disk.

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<sup>17</sup>. These absorption data tabulated in Table-1 are separately analyzed through various correlation equations. The results of the statistical analysis<sup>18</sup> are presented in Table-2.

TABLE-1  
*s-cis* AND *s-trans* CARBONYL STRETCHING FREQUENCIES ( $\text{cm}^{-1}$ ) OF  
SUBSTITUTED STYRYL-2-NAPHTHYL KETONES

Substituent	<i>s-cis</i> $\nu(\text{CO}) (\text{cm}^{-1})$	<i>s-trans</i> $\nu(\text{CO}) (\text{cm}^{-1})$
H	1628	1662
<i>m</i> -NH <sub>2</sub>	1627	1661
<i>p</i> -NH <sub>2</sub>	1622	1657
<i>m</i> -Br	1624	1659
<i>m</i> -Cl	1622	1663
<i>p</i> -Cl	1632	1669
<i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>	1620	1656
<i>p</i> -OH	1625	1666
<i>p</i> -OCH <sub>3</sub>	1626	1660
<i>p</i> -CH <sub>3</sub>	1625	1661
<i>o</i> -NO <sub>2</sub>	1635	1670
<i>m</i> -NO <sub>2</sub>	1630	1676
<i>p</i> -NO <sub>2</sub>	1626	1666

TABLE-2  
RESULTS OF STATISTICAL ANALYSIS OF CARBONYL STRETCHING  
FREQUENCIES OF SUBSTITUTED STYRYL-2-NAPHTHYL KETONES

Carbonyl frequency correlated	Constant for correlation	<i>r</i>	<i>I</i>	$\rho$	<i>s</i>	<i>n</i>	Substituent in styryl part
<i>s-cis</i>	$\sigma$	0.958	1663.8	9.21	8.20	13	H, <i>m</i> -HN <sub>2</sub>
	$\sigma^+$	0.835	1664.0	5.37	9.40	13	<i>p</i> -NH <sub>2</sub> , <i>m</i> -Br
	$\sigma_1$	0.903	1658.4	18.81	9.00	13	<i>m</i> -Br
	$\sigma_R$	0.880	1667.7	14.36	1.95	13	<i>p</i> -Cl, and <i>p</i> -N(CH <sub>3</sub> ) <sub>2</sub>
<i>s-trans</i>	$\sigma$	0.997	1627.5	7.93	4.27	13	<i>p</i> -OH,
	$\sigma^+$	0.879	1628.0	4.13	5.00	13	<i>p</i> -CH <sub>3</sub> , <i>p</i> -CH <sub>3</sub>
	$\sigma_1$	0.759	1618.7	26.20	6.57	13	<i>p</i> -CH <sub>3</sub> , <i>o</i> -NO <sub>2</sub> ,
	$\sigma_R$	0.890	1628.5	9.10	5.10	13	<i>m</i> -NO <sub>2</sub> , <i>p</i> -NO <sub>2</sub>

The analysis of the data in Table-2 reveals that the substituent effect is good correlated with Hammett  $\sigma$  constants and  $\sigma_1$  is satisfactory for the *s-cis* carbonyl stretching and only  $\sigma$  constants for *s-trans* conformers. The correlations with  $\sigma^+$  for these frequencies in *s-trans* and *s-cis* are not significant. This demonstrates that in these conformers there is steric repulsion and the co-planarity between the styryl and the naphthyl parts is largely affected. However, the expected conjugation between  $-\text{CH}=\text{CH}-$  and  $\text{C}=\text{O}$  group is missing in the conformers. Therefore  $\sigma^+$  constants do not produce satisfactory correlation with the carbonyl frequencies.

In view of the inability of some of the  $\sigma$  constants to produce individually satisfactory correlations, it was thought worth while to seek multiple correlations involving either  $\sigma_1$  and  $\sigma_R$  constants or Swain-Lupton's<sup>19</sup> constants F and R parameters. The correlation equations are generated in Table-3. From the equations it is inferred that the correlation is good with  $\sigma_1$  and  $\sigma_R$  and F and R parameters together.

TABLE-3  
RESULTS OF STATISTICAL ANALYSIS OF CARBONYL STRETCHING  
FREQUENCIES WITH  $\sigma_1$  &  $\sigma_R$  AND F & R PARAMETERS

Conformers	Parameters	Correlation Equations	Substituents
<i>s-cis</i>	$\sigma_1$ & $\sigma_R$	1664.2 + 14.22 $\sigma_1$ + 24.33 $\sigma_R$	H
		( $\pm 11.73$ )( $\pm 2.224$ )( $\pm 4.671$ )	<i>m</i> -NH <sub>2</sub>
		(R = 0.972 n = 13, P > 90%)	<i>p</i> -NH <sub>2</sub>
	F & R	1668.3 + 15.26F + 19.43R	<i>m</i> -Br
( $\pm 4.721$ )( $\pm 3.270$ )( $\pm 7.490$ )		<i>m</i> -Cl, <i>p</i> -Cl	
	(R = 0.920, n = 13, P > 90%)	<i>p</i> -(NCH <sub>3</sub> ) <sub>2</sub>	
<i>s-trans</i>	$\sigma_1$ & $\sigma_R$	1618.32 + 13.221 $\sigma_1$ + 13.01 $\sigma_R$	<i>p</i> -OH
		( $\pm 7.11$ )( $\pm 0.572$ )( $\pm 0.724$ )	<i>p</i> -OCH <sub>3</sub>
		(R = 0.998, n = 13, P > 90%)	<i>p</i> -CH <sub>3</sub>
	F & R	1620.00 + 13.52F + 14.00R	<i>o</i> -NO <sub>2</sub>
( $\pm 4.521$ )( $\pm 3.770$ )( $\pm 4.490$ )		<i>m</i> -NO <sub>2</sub>	
	(R = 0.920, n = 13, P > 90%)	<i>p</i> -NO <sub>2</sub>	

## REFERENCES

1. W.F. Winecoff and D.W. Boykin (Jr.), *J. Org. Chem.*, **37**, 674 (1972).
2. R.S. Mulliken, *J. Chem. Phys.*, **7**, 121 (1939).
3. L.J. Bellamy, *J. Chem. Soc.*, 2828 (1955).
4. ———, *J. Chem. Soc.*, 4221 (1955).
5. M. St. C. Flett, *Trans. Faraday Soc.*, **44**, 767 (1948).
6. W.H.T. Davison, *J. Chem. Soc.*, 2456 (1951).
7. N. Fuson, M.L. Josein and E.M. Shelton, *J. Am. Chem. Soc.*, **6**, 2526 (1954).
8. G.K. Das, *Indian J. Chem.*, **40A**, 23 (2001).

9. A. Macioni and Marongin, *Ann. Chim.*, **50**, 1806 (1960).
10. S. Sukhwai, A. Ashawa and B.L. Verma, *Asian J. Chem.*, **7**, 615 (1995).
11. L. Bensignore, S. Cabiddu, A. Maccioni and E. Maroogive, *Gazz. Chem. (Ital.)*, **106**, 617 (1976).
12. M. Apparao, A. Nayak and M.K. Rout, *J. Inst. Chem.*, **44**, 151 (1971).
13. H.J. Williams and R.G. Shelter, *Aust. J. Chem.*, **27**, 685 (1974).
14. S.S. Misra and K. Dinkar, *J. Indian Chem. Soc.*, **52**, 556 (1975).
15. K. Rajesekaran and C. Gnanasekaran, *Indian J. Chem.* **25A**, 64 (1986).
16. \_\_\_\_\_, *J. Chem. Soc. Perkin Trans. II*, 263 (1987).
17. W.P. Hays and C.J. Tommons, *Spectrochim. Acta*, **24A**, 323 (1968).
18. G.W. Snedecor and W.G. Cochran, *Statistical Methods*, Iowa State University Press, Ames, Iowa (1967).
19. C.G. Swain and E.C. Lupton (Jr.), *J. Am. Chem. Soc.*, **90**, 4329 (1968).

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