

Substituent Effects on Carbonyl Stretching Frequency of β -Naphthyl Styryl Ketones

K RAJASEKARAN & C GNANASEKARAN*

Postgraduate Department of Chemistry, VHNSN College,
Virudhunagar 626001

Received 13 December 1984, revised and accepted 25 June 1985

The *s-cis* carbonyl stretching frequencies of two series of substituted β -naphthyl styryl ketones have been measured in chloroform and carbon tetrachloride. One series contains substituents in benzene ring (Series-A) and the other contains substituents in naphthalene ring (Series-B). Substituent effects have been analysed in terms of Hammett equation. Good correlations have been obtained with σ_p^+ constants in both the solvents. The low ρ -value for Series-A as compared to that of chalcones is explained on the basis of non-coplanarity of the styryl group and the carbonyl group in the ketones of Series-A.

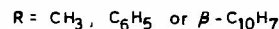
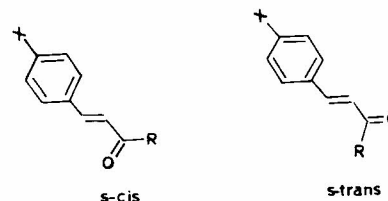
In recent years much attention has been paid to correlate the infrared group frequencies of related group of organic molecules with substituent constants¹. Good correlations have been obtained for $\nu\text{C}=\text{O}$ with the substituent constants, σ_p^+ in the case of acetophenones², benzophenones³, chalcones⁴ and benzalacetones⁵. However, similar studies in polynuclear aromatic system are lacking. With a view to understanding the extent of transmission of electronic effects of the substituents in naphthalene system, several 6'-substituted β -naphthyl styryl ketones (Series-B) and 4-substituted β -naphthyl styryl ketones (Series-A) were prepared and their carbonyl stretching frequencies were measured in chloroform and carbon tetrachloride.

The 6-substituted 2-acetonaphthones were prepared by literature method⁶. The benzaldehydes were commercial samples (Fluka, AR). β -Naphthyl styryl ketones were prepared by Claisen-Schmidt condensation⁷ of appropriate aldehydes and ketones and recrystallised from benzene-pet ether (60-80°).

Spectral grade chloroform was passed through alumina before use and carbon tetrachloride was dried over anhydrous potassium carbonate and distilled in an all glass apparatus. The $\nu\text{C}=\text{O}$ were measured at 25° with a Perkin-Elmer IR-783 double beam grating spectrophotometer using CsI cells of 1 mm path length. The IR spectra of the compounds were recorded in CHCl_3 and CCl_4 at concentrations of 0.5% and 0.2% respectively. The β -naphthyl styryl ketones exhibited a shoulder on the lower frequency side of the band. The height of each band was taken as the

distance from shoulder to the point of maximum absorption. The band frequencies were then measured at the half-width of the half-height of the band. The frequencies were directly read from the digital display corresponding to this position. The values reported here are average of three scans which are accurate within $\pm 0.2\text{cm}^{-1}$.

The α,β -unsaturated ketones exist in two different conformations namely *s-cis* and *s-trans*. The carbonyl



stretching frequencies of these conformers (1665cm^{-1} for *s-cis* and 1639cm^{-1} for *s-trans* conformer) have been assigned for chalcone in chloroform⁸. In the present study the assignments have been made by analogy. In chloroform all β -naphthyl styryl ketones exhibited an intense band near 1662cm^{-1} with a shoulder at the lower frequency side of the band. This band was assigned to the *s-cis* conformer. It was difficult to identify the non-*s-cis* band for various substituted β -naphthyl styryl ketones since the intensity and shape of this band was similar to the aromatic hydrogen overtone bands in the 1600cm^{-1} region. The parent ketone exhibited a broad, weak band at 1629cm^{-1} which was assigned to the *s-trans* or non-*s-cis* conformer. A shift of approximately 6cm^{-1} was observed for the *s-cis* carbonyl band on changing the solvent from chloroform to carbon tetrachloride. This may be due to weak hydrogen bonding between carbonyl group and the solvent molecules (chloroform).

Effect of substituents in benzene ring (Series-A)

The $\nu\text{C}=\text{O}$ modes of the *s-cis* conformers of several 4-substituted β -naphthyl styryl ketones are presented in Table 1. These modes were correlated with σ_p/σ_p^+ constants. The results of statistical analysis are presented in Table 2. The $\nu\text{C}=\text{O}$ modes were found to correlate better with σ_p^+ constants. The low ρ -values obtained in both the solvents do not differ much. Apparently, weak hydrogen bonding in chloroform does not have a large influence on the transmission of substituent effects. Analysis of the data in Table 2 reveals that the ρ -values in both solvents are lower

Table 1—*s-cis* Carbonyl Stretching Frequencies of Substituted β -Naphthyl Styryl Ketones

Substituent	Series-A		Substituent	Series-B	
	$\nu\text{C}=\text{O}(\text{cm}^{-1})$			$\nu\text{C}=\text{O}(\text{cm}^{-1})$	
	CHCl_3	CCl_4		CHCl_3	CCl_4
4-N(CH ₃) ₂	1653.7	1660.5	6'-OCH ₃	1659.0	1665.5
4-OCH ₃	1658.4	1665.3	6'-SCH ₃	1659.9	1666.5
4-CH ₃	1660.5	1666.7	6'-CH ₃	1661.3	1667.0
4-H	1662.0	1668.0	6'-H	1662.0	1668.0
4-F	1662.5	1668.3	6'-F	1662.5	1668.6
4-Cl	1663.8	1669.0	6'-Cl	1663.0	1668.9
4-Br	1663.0	1668.6	6'-Br	1662.8	1668.8
4-NO ₂	1665.5	1671.2	6'-I	1662.9	1668.7
			6'-CN	1664.9	1670.6

Table 2—Results of Statistical Analysis of Carbonyl Stretching Frequencies with σ_p/σ_p^+ Constants

σ -constants	ρ	$i(\text{cm}^{-1})$	r	S.O.
	Series-A: Solvent CHCl_3			
σ_p	7.50	1661.0	0.966	1.01
σ_p^+	4.86	1662.2	0.996	0.36
	Series-A: Solvent CCl_4			
σ_p	6.68	1667.2	0.970	0.85
σ_p^+	4.30	1668.3	0.994	0.37
	Series-B: Solvent CHCl_3			
σ_p	5.64	1661.3	0.891	0.85
σ_p^+	3.98	1662.3	0.987	0.30
	Series-B: Solvent CCl_4			
σ_p	4.66	1667.5	0.904	0.65
σ_p^+	3.21	1668.3	0.977	0.30
	Chalcone ^a : Solvent CHCl_3			
σ_p^+	6.24	1666.7	0.977	0.77
	Chalcone: Solvent CCl_4			
σ_p^+	5.36	1670.5	0.988	0.40

(a) Ref. 4

than those of 3- and 4-substituted chalcones⁴. It appears that significant amount of difference in transmission of electronic effects of the substituents may arise from the differences in the coplanarity of the styryl group and the carbonyl group. In the case of *s-cis* conformer, the R group and the α -hydrogen are in close proximity and their interaction should alter the coplanarity of the styryl group and the carbonyl group. If the R group is smaller, there will be less interaction between it and the α -hydrogen and hence it would be possible for a greater degree of coplanarity to be achieved. On the other hand, if the R group is bulky, the extent of coplanarity will be decreased and hence the transmission of the electronic effects of substituents will be reduced. The ratio of ρ -values of chalcone and β -naphthyl styryl ketone is 0.85 and this indicates that in the present case, the transmission of electronic effects is only 85%, compared to chalcone.

Effect of substituents in naphthalene ring (Series-B)

In order to understand the extent of transmission of electronic effects of the substituents across the naphthalene ring, the $\nu\text{C}=\text{O}$ modes of the *s-cis* conformers of several 6'-substituted β -naphthyl styryl ketones were measured (Table 1). The 2'- and 6'-positions in naphthalene ring are analogous to the *para*-position in benzene system and hence $\nu\text{C}=\text{O}$ were correlated with σ_p/σ_p^+ constants (Table 2). For *s-cis* conformers of 3'- and 4'-substituted chalcones⁴, the ρ -value was 5.44 in chloroform solvent. The ρ -value for naphthalene system is lower and this may be due to the fact that the electronic effects of the substituents are to be transmitted from one ring to another ring. Unlike in the case of chalcones, the correlation with σ_p^+ constants is fairly good. This may be due to the fact that for β -naphthyl styryl ketones, there may be a constant average conformation, i.e. the extent of coplanarity may not be changing with substituents, unlike for chalcones where coplanarity of the styryl group and the carbonyl group may be affected by the introduction of substituents.

Good correlation with σ_p^+ constants implies that there is significant resonance interaction between the substituents and the carbonyl group and hence the carbonyl frequencies were analysed in terms of Yukawa-Tsuno equation⁹. Multiple linear regression analysis gave the following equations.

For Series-A in CCl_4 and CHCl_3 respectively

$$\nu\text{C}=\text{O} = 4.25\sigma_p + 4.38(\sigma_p^+ - \sigma_p) + 1668.2 \text{ cm}^{-1} (r = 0.992)$$

$$\nu\text{C}=\text{O} = 4.49\sigma_p + 5.43(\sigma_p^+ - \sigma_p) + 1662.3 \text{ cm}^{-1} (r = 0.994)$$

For Series-B in CCl_4 and CHCl_3 respectively

$$\nu\text{C}=\text{O} = 3.39\sigma_p + 2.98(\sigma_p^+ - \sigma_p) + 1668.2 \text{ cm}^{-1} (R = 0.971)$$

$$\nu\text{C}=\text{O} = 3.98\sigma_p + 3.98(\sigma_p^+ - \sigma_p) + 1662.3 \text{ cm}^{-1} (r = 0.983).$$

The quantity r^+ gives the contribution of the enhanced resonance effect of $+K$ substituents. The magnitude of r^+ is 1.2 and 1.0 respectively for Series-A and B in chloroform. The magnitude of r^+ for Series-B indicates that there is considerable resonance interaction between substituents and the carbonyl group even though they are present in different rings.

The authors express their thanks to Prof P. Ananthakrishnan, Anna University, Madras for his encouragement and authorities of Managing Board of VHNSN College, Virudhunagar for research facilities. One of the authors (CG) also thanks the DST, New Delhi for a research grant.

References

- 1 *Advances in linear free energy relationship*, edited by N B Chapman & J Shorter (Plenum Press, London), 1972, Chapter 3.
- 2 Jones R N, Forbes W F & Mueller W A, *Can J Chem*, **35** (1957) 504; Krueger P J, *Can J Chem*, **51** (1973) 1363.
- 3 Fuson N, Josien M L & Shelton E M, *J Am chem Soc*, **76** (1954) 2526.
- 4 Silver N L & Boykin D W, *J org Chem*, **35** (1970) 759.
- 5 Winecoff W F & Boykin D W, *J org Chem*, **37** (1972) 674.
- 6 Ananthakrishna Nadar P, Gnanasekaran C & Chandrasekaran J, *J chem Res (S)*, (1978) 424.
- 7 Macioni A & Marongin E, *Ann Chim*, **50** (1960) 1806.
- 8 Hayes W P & Timmons C J, *Spectrochim Acta*, **24A** (1968) 323.
- 9 Yukawa Y & Tsuno Y, *Bull chem Soc Japan*, **32** (1959) 971.