Influence of Conformation on Transmission of Electronic Effects of Substituents. Correlation of Infrared Carbonyl Stretching Frequencies of 4-Substituted α-Naphthyl Styryl Ketones

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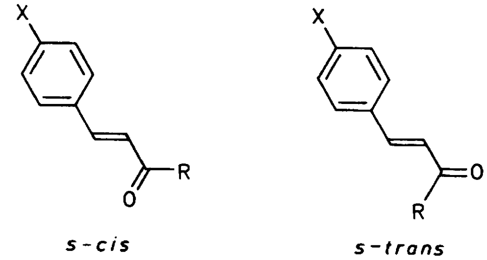
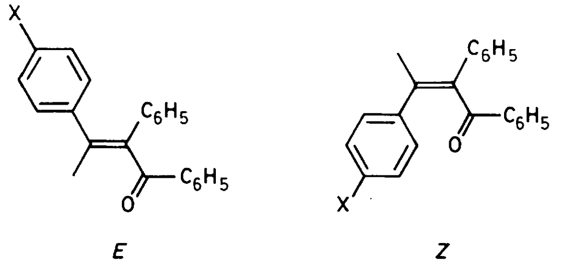
The *s-cis* and *s-trans* carbonyl stretching frequencies of several 4-substituted α-naphthyl styryl ketones have been measured in carbon tetrachloride and chloroform. The carbonyl stretching frequencies correlate very well with σ^+ constants. The low ρ_{cis}/ρ_{trans} ratio obtained for the present system compared with benzylideneacetones and chalcones shows that for effective transmission of the electronic effects of the substituents, the styryl group and the carbonyl group must be coplanar. Comparison of the attenuation factors, π_Y and $\pi_{R'}$, for different α,β-unsaturated ketones also supports this idea.

In recent years much attention has been paid to the influence of conformation and configuration on the transmission of electronic effects of the substituents in α,β-unsaturated ketones.[1–7] The α,β-unsaturated ketones exist in two different conformations namely *s-cis* and *s-trans*. The influence of conformation on the transmission of electronic effects of the substituents has been investigated by measuring the i.r. carbonyl stretching frequencies of *s-cis* and *s-trans* conformers in solution. Perjéssy[2] studied the substituent effects on the carbonyl stretching frequencies of chalcones and concluded that the *s-trans* conformers transmit the electronic effects of the substituents more effectively than the *s-cis* conformers on the basis of the magnitude of the ρ values. Examination of steric models shows that in the case of an *s-cis* conformer, the R group and the α-hydrogen are in close proximity and their steric interaction will reduce the degree of coplanarity of the styryl and carbonyl groups. An important mode for transmission of the electronic effects of substituents is by resonance. For effective conjugation, the styryl group and the carbonyl group must be coplanar. In *s-cis* conformers, the degree of coplanarity is lower than that of the *s-trans* conformers and hence the former transmits electronic effects of the substituents to a lesser amount. If the degree of coplanarity is an important factor in determining the transmission ability, it may be expected that as the R group becomes smaller in size, both conformers would have nearly equal ρ values. Thus in benzylideneacetones,[3] where R is a small methyl group, the ρ values were found to be nearly equal for both conformers (Table 3). These results suggest that the transmission ability and the degree of coplanarity are interlinked.

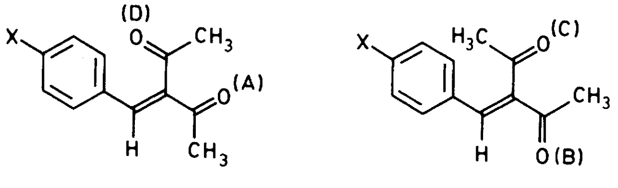
The alteration of the transmission of electronic effects through an intervening link by changing the geometric relationship has been studied for α-phenylchalcones (IV).[4] The steric interaction of the 3-aryl group with the benzoyl group in the *Z*-isomer results in deconjugation of the carbonyl group and the styryl group and the *Z*-series is insensitive to substituent effects (ρ 1.10). On the other hand, the *E*-series is much more sensitive to substituent effects (ρ 6.35). A recent study by Perjéssy and Hrnicar[6] on the correlation of the i.r. carbonyl stretching frequencies of substituted benzylidenepentane-2,4-dione (V) is also in accord with the above facts. The vibrational frequencies of *E-s-trans* (A) and *E-s-cis* (B) are very sensitive to substituent effects (ρ 7.74 and 5.19 for *E-s-trans* and *E-s-cis* series respectively in CCl_4). The carbonyl groups (A) and (B) are nearly coplanar. On the other hand the vibrational frequencies of the *Z-s-trans* (D) series, where the carbonyl group is twisted out of the plane of the C=C double bond by *ca.* 60°, are very weakly sensitive to the substituent effects (ρ 1.97). This is due to broken conjugation between the benzylidene moiety and carbonyl group (D).



(I) R = CH_3
(II) R = C_6H_5
(III) R = α-$C_{10}H_6I$

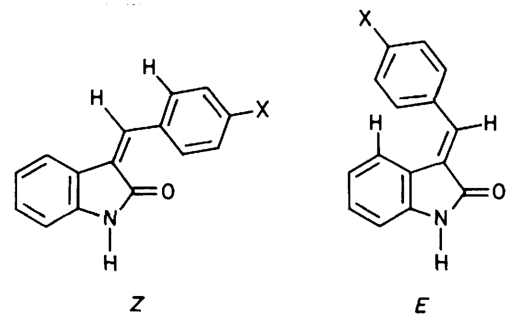


(IV)



(V)

However the results obtained from the configurational isomers of arylidene-1,3-dihydroindol-2-ones (VI)[7] are conflicting. In the *Z*-isomer the aryl group and the carbonyl group are coplanar whereas in the *E*-isomer the dihedral angle between C=C–C=O and the aryl system is 49°. The ρ values for the carbonyl stretching frequencies were found to be 8.03 and 10.07 for *Z*- and *E*-isomers, respectively. The twisted conformation of the *E*-isomers does not prevent the transmission of the electronic effects by resonance, *i.e.* conjugation is still possible



(VI)

Table 1. Analytical data for 4-substituted 4′-iodo-α-naphthyl styryl ketones (III)

Substituent X	Formula	M.p. (°C)	Found (%) (Required) C	H
4-N(CH$_3$)$_2$	$C_{21}H_{18}INO$	138—139	59.2 (59.0)	4.1 (4.2)
4-OCH$_3$	$C_{20}H_{15}IO_2$	112—113	58.0 (57.8)	3.7 (3.6)
4-CH$_3$	$C_{20}H_{15}IO$	124—125	60.1 (60.3)	3.8 (3.8)
4-H	$C_{19}H_{13}IO$	120—121	59.4 (59.3)	3.3 (3.4)
4-F	$C_{19}H_{12}FIO$	128—129	57.0 (56.7)	3.8 (3.0)
4-Cl	$C_{19}H_{12}ClIO$	129—130	54.7 (54.5)	2.8 (2.9)
4-Br	$C_{19}H_{12}BrIO$	135—136	49.4 (49.2)	2.7 (2.6)
4-NO$_2$	$C_{19}H_{12}INO_3$	152—153	53.3 (53.1)	2.9 (2.8)

Table 2. *s-cis* and *s-trans* carbonyl stretching frequencies of 4-substituted 4′-iodo-α-naphthyl styryl ketones (III)

Substituent X	$\tilde{\nu}^a_{C=O}$/cm^{-1} *s-cis*	*s-trans*	$\tilde{\nu}^b_{C=O}$/cm^{-1} *s-cis*	*s-trans*
N(CH$_3$)$_2$	1 655.6	1 628.2	1 663.3	1 638.6
OCH$_3$	1 658.2	1 633.4	1 667.0	1 643.5
CH$_3$	1 660.1	1 636.6	1 668.1	1 647.6
H	1 662.6	1 640.6	1 669.8	1 649.0
F	1 663.0	1 641.0	1 670.2	1 649.6
Cl	1 664.0	1 641.4	1 671.2	1 649.8
Br	1 663.8	1 641.6	1 671.0	1 649.7
NO$_2$	1 667.0	1 647.5	1 673.6	1 656.0

[a] Chloroform. [b] Carbon tetrachloride.

even if the system deviates considerably from planarity.[8,9] Therefore it was suggested that the carbonyl frequency cannot be recommended as a basis for determining the degree of coplanarity of α,β-unsaturated ketones.

In the present study several 4-iodo-α-naphthyl 4-substituted styryl ketones (III) were prepared and the carbonyl stretching frequencies of the *s-cis* and *s-trans* conformers were measured in chloroform and carbon tetrachloride with a view to gaining further information regarding the influence of conformation on the transmission of electronic effects of the substituents.

Experimental

4-*Iodo*-1-*acetonaphthone*.—This was prepared by the Friedel–Craft acylation of 1-iodonaphthalene by the method of Jacops *et al.*[10] The product crystallised from ethanol and melted at 72—73 °C (Found: C, 48.9; H, 2.8. $C_{12}H_9IO$ requires C, 48.7; H, 3.1%).

4′-*Iodo-α-naphthyl Styryl Ketones* (**III**).—The α-naphthyl styryl ketones (**III**) were prepared by treating a mixture of 4-iodo-1-acetonaphthone (0.01 mol) and the appropriate aldehyde (0.01 mol) in ethanol (50 ml) in the presence of 10% sodium hydroxide solution (5 ml). All the compounds were recrystallised from benzene–light petroleum (b.p. 60—80 °C) and characterised by elemental analysis (Table 1).

Spectral grade carbon tetrachloride was dried over anhydrous potassium carbonate and fractionated. Spectral grade chloroform was dried over P_2O_5 and passed through alumina column and the middle fraction was collected.

I.r. spectra of ketones (**III**) were recorded with a Perkin-Elmer IR-783 double-beam grating spectrophotometer at 25 °C using CsI matched cells of 1 mm path length. The concentration of ketones was *ca.* 0.5% and 0.2% in carbon tetrachloride and chloroform, respectively. Ketones (**III**) exhibit a shoulder on the lower frequency side of the band. The height of each band was taken as the distance from the 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 reported here are the average of three scans which are accurate to within ± 0.2 cm^{-1}. Calibrations were made using polystyrene peaks.

Results and Discussion

The carbonyl stretching frequencies for *s-cis* and *s-trans* conformers have been assigned for chalcone[11] in chloroform. The intense band at 1 665 cm^{-1} was assigned to the *s-cis* conformer and the broad band of much weaker intensity at 1 639 cm^{-1} to the *s-trans* conformer. These assignments were

Table 3. Regression analysis data using σ^+ constants

System	Conformer	Solvent	ρ	ν_0/cm^{-1}	*r*	*s*	Ref.
Benzylideneacetone	*s-cis*	CCl$_4$	5.38 ± 0.17	1 697.9 ± 0.1	0.995	0.48	*a*
Benzylideneacetone	*s-trans*	CCl$_4$	6.22 ± 0.32	1 675.9 ± 0.3	0.984	0.98	*a*
Chalcone	*s-cis*	CHCl$_3$	6.18 ± 0.25	1 666.7 ± 0.1	0.985	0.60	*b*
Chalcone	*s-trans*	CHCl$_3$	8.23 ± 0.50	1 641.9 ± 0.1	0.985	1.20	*b*
Chalcone	*s-cis*	CCl$_4$	5.62 ± 0.48	1 673.7 ± 0.3	0.972	1.10	*b*
Chalcone	*s-trans*	CCl$_4$	7.20 ± 0.34	1 654.2 ± 0.2	0.991	0.80	*b*
(III)	*s-cis*	CHCl$_3$	4.71 ± 0.26	1 662.9 ± 0.2	0.981	0.74	*c*
(III)	*s-trans*	CHCl$_3$	7.89 ± 0.35	1 640.6 ± 0.3	0.988	1.00	*c*
(III)	*s-cis*	CCl$_4$	4.20 ± 0.16	1 670.2 ± 0.1	0.991	0.45	*c*
(III)	*s-trans*	CCl$_4$	6.83 ± 0.28	1 649.5 ± 0.2	0.989	0.78	*c*

[a] Ref. 3. [b] Ref. 5. [c] Present study.

made on the basis of solvent dependency. The i.r. spectrum of (**III**; X = H) in chloroform exhibits an intense band near 1 662 cm^{-1} with a shoulder on the lower frequency side of the band. In carbon tetrachloride, a similar band appears at 1 670 cm^{-1}. These bands have been assigned to the *s-cis* conformer. A low intense band with a shoulder on the lower frequency side is observed near 1 641 and 1 649 cm^{-1} in chloroform and carbon tetrachloride, respectively. These bands are assigned to *s-trans* conformer. These assignments were made only by analogy. The carbonyl stretching frequencies of *s-trans* conformers occur at lower frequency due to the more extended conjugation possible in this conformer.

The carbonyl stretching frequencies of *s-cis* and *s-trans* conformers of several 4-substituted ketones (**III**) in chloroform and carbon tetrachloride are presented in Table 2. A shift of *ca.* 8 cm^{-1} was observed on changing the solvent from chloroform to carbon tetrachloride. This may be due to weak hydrogen bonding between the carbonyl group and solvent chloroform.

Electron-releasing substituents lower the carbonyl stretching frequency whereas electron-attracting substituents increase it. The carbonyl stretching frequencies were correlated with σ^+ constants and the results of regression analysis are presented in Table 3 together with the data for chalcones and benzylideneacetones. Satisfactory correlations were obtained with σ^+ constants and this implies that there is a considerable amount of resonance between the substituents and the carbonyl group. The ρ values obtained in both the solvents do not differ very much. This shows that the weak hydrogen bonding in chloroform does not have much influence on the transmission of electronic effects of the substituents.

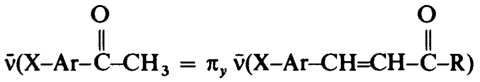
Table 4. $\rho_{cis}:\rho_{trans}$ ratio for α,β-unsaturated ketones

System	Solvent	ρ_{cis}	ρ_{trans}	$\rho_{cis}:\rho_{trans}$	Ref.
Benzylideneacetone	CCl_4	5.38	6.28	0.86	*a*
Chalcone	CCl_4	5.62	7.20	0.78	*b*
Chalcone	$CHCl_3$	6.18	8.23	0.76	*b*
(**III**)	CCl_4	4.20	6.83	0.61	*c*
(**III**)	$CHCl_3$	4.71	7.89	0.60	*c*

[a] Data from ref. 3. [b] Data from ref. 5. [c] Present study.

The relative ability to transmit electronic effects of the substituents by *s-cis* and *s-trans* conformers may be understood from the $\rho_{cis}:\rho_{trans}$ ratio. Table 4 lists this ratio for different α,β-unsaturated ketones. The lower $\rho_{cis}:\rho_{trans}$ ratio obtained for ketones (**III**) compared with chalcones and benzylideneacetones reveals that the steric requirement of the α-naphthyl group is somewhat greater than that of the methyl and phenyl groups. It is interesting to note that the ρ_{trans} value for (**III**) is nearly equal to that for chalcones (Table 4). On the other hand, the ρ_{cis} value for (**III**) is significantly less than the ρ_{cis} value for chalcones. Since the α-naphthyl styryl group is bulkier than the phenyl group, in (**III**) the degree of coplanarity of the group and carbonyl groups will be less than the chalcones. These results show that the degree of coplanarity of the styryl group and the carbonyl group is an important factor in determining the extent of transmission of electronic effects of the substituents in α,β-unsaturated ketones.

The effect of introduction of a double bond on the transmission of electronic effects of the substituents in the phenyl group to the vibrating carbonyl group can be analysed by equation (1). Here π_y is the ratio $\rho_{ArCOCH_3}:\rho_{ArCH=CH-CO-R}$ which is determined without involving empirical σ constants. Analysis of carbonyl stretching frequencies in terms of equation (1) gives the overall attenuation of the electronic effects of the substituents.

 (1)

$$\bar{\nu}(\text{X–Ar–}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{–CH}_3) = \pi_y\,\bar{\nu}(\text{X–Ar–CH=CH–}\overset{\text{O}}{\overset{\|}{\text{C}}}\text{–R}) \qquad (1)$$

The attenuation factors, π_y, for different α,β-unsaturated ketones are presented in Table 5. The carbonyl stretching frequencies of substituted acetophenones used in the correlation were those of Laurence and Berthelot.[12] The data indicate that in general π_y for the *s-cis* conformers is less than that for *s-trans.*

Azzarro *et al.*[13] have analysed the carbonyl stretching frequencies of α,β-unsaturated ketones by the dual-substituent

Table 5. Attenuation factor π_y for α,β-unsaturated ketones

System	Solvent	Conformer	π_y	*r*	*s*	n^a
Benzylideneacetone	CCl_4	*s-cis*	0.49 ± 0.02	0.991	0.63	8
Benzylideneacetone	CCl_4	*s-trans*	0.57 ± 0.03	0.983	1.00	8
Chalcone	$CHCl_3$	*s-cis*	0.58 ± 0.02	0.994	0.57	9
Chalcone	$CHCl_3$	*s-trans*	0.77 ± 0.04	0.983	1.34	8
(**III**)	CCl_4	*s-cis*	0.38 ± 0.01	0.990	0.47	8
(**III**)	CCl_4	*s-trans*	0.61 ± 0.02	0.991	0.76	8
(**III**)	$CHCl_3$	*s-cis*	0.42 ± 0.02	0.983	0.71	8
(**III**)	$CHCl_3$	*s-trans*	0.71 ± 0.03	0.991	0.88	8

[a] *n* = number of data used.

Table 6. Dual-substituent parameter analysis data of carbonyl stretching frequencies of α,β-unsaturated ketones and attenuation factor, π_R

System	Solvent	Conformer	ρ_I	ρ_R	*r*	π_R	n^b
Benzylideneacetone	CCl_4	*s-cis*	5.71 ± 1.10	5.28 ± 0.48	0.993	0.47	8
Benzylideneacetone	CCl_4	*s-trans*	8.48 ± 1.68	5.59 ± 0.73	0.988	0.52	8
Chalcone	$CHCl_3$	*s-cis*	7.80 ± 0.72	5.91 ± 0.30	0.996	0.55	9
Chalcone	$CHCl_3$	*s-trans*	7.00 ± 2.00	8.82 ± 0.81	0.986	0.83	8
(**III**)	$CHCl_3$	*s-cis*	6.72 ± 0.90	4.18 ± 0.33	0.990	0.39	8
(**III**)	$CHCl_3$	*s-trans*	10.38 ± 1.67	7.26 ± 0.60	0.988	0.68	8
(**III**)	CCl_4	*s-cis*	5.67 ± 0.44	3.81 ± 0.16	0.997	0.36	8
(**III**)	CCl_4	*s-trans*	7.43 ± 1.34	6.66 ± 0.49	0.990	0.62	8
Acetophenone^a	CCl_4		12.13 ± 0.86	10.69 ± 0.34	0.998		8

[a] Data from ref. 12. [b] *n* = number of data used.

parameter equation (2).[14] They have defined the attenuation

$$\bar{\nu} - \bar{\nu}_0 = \rho_I\sigma_I + \rho_R\sigma_R \qquad (2)$$

factor for aromatic systems as follows: $\pi_I = \rho_I(X)/\rho_T$(PhCOMe); $\pi_R = \rho_R(X)/\rho_R$(PhCOMe) where X is an α,β-unsaturated ketone. This type of analysis enables one to understand the attenuation of inductive and resonance effects separately. The carbonyl stretching frequencies of benzylideneacetones, chalcones, and **(III)** were analysed by equation (2) and the results of regression analysis are presented in Table 6. The σ_I and σ_R constants used in the correlations are those employed by Brownlee and Topsom.[15] It is seen that the π_R values are almost the same for the *s-cis* and *s-trans* conformers in the case of benzylideneacetones. For chalcones and **(III)**, the π_R values for *s-cis* conformers are found to be less than those for the *s-trans*. Further, the π_R value for the *s-cis* conformer **(III)** is less than that for chalcones. These observations are in accord with the fact that for effective transmission of electronic effects of the substituents by resonance, the styryl and carbonyl groups must be coplanar.

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