

## Conformational analysis of cinnamanilides

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**Abstract.** The conformational analysis of cinnamanilides has been carried out using IR spectroscopy. All the anilides studied were found to exist as equilibrium mixtures of *s-cis* and *s-trans* forms in benzene.

The *s-cis* form was predominant over the *s-trans* in all the anilides except in the *p*-nitro anilide in which the *s-trans* form was predominant. The relative stabilities of the conformers were found to depend upon the electrostatic repulsions between the anilide nitrogen and the  $\beta$ -carbon atom in the *s-trans* form and those between the  $\pi$ -electrons of the C=O and C=C bonds in the *s-cis* form.

**Keywords.** Cinnamanilides; *s-cis* and *s-trans* forms; stability of conformers;  $\beta$ -carbon and nitrogen atoms; electrostatic repulsions.

### 1. Introduction

In continuation of our study on the influence of varying degrees of C=O bond polarisation on the stabilities of the conformations of  $\alpha, \beta$ -unsaturated carbonyl compounds (Venkateshwarlu and Subrahmanyam 1988, 1990). We report in this communication the conformations of cinnamanilides and their relative stabilities.

### 2. Experimental

#### 2.1 Materials

The cinnamanilides were prepared by the method given by Vogel (1980) from cinnamoyl chloride and the substituted anilines in benzene. The solids obtained were recrystallised twice from methanol and were TLC pure. The solvents used in the study were purified by standard methods available in literature and were distilled before use and only the middle fractions were collected.

#### 2.2 Measurement of the spectra

The IR spectra of equimolar solutions (M/20) of the samples in solvents of varied dielectric constants were recorded on a Shimadzu-400 grating double beam spectro-

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photometer at 28°C using NaCl matched cells of 0.1 mm path length. The wave number scale was expanded by a factor of four and the spectra were calibrated by using polystyrene film. Extensive overlap of the two bands prevented measurement of their integrated intensities. The relative populations of the two conformers were, therefore, estimated by measuring the apparent optical densities of the C=O bands as was done in many investigations earlier (Erskine and Waight 1960; Hayes and Timmons 1968; Venkateshwarlu and Subrahmanyam 1987, 1988, 1990).

### 3. Results and discussion

All the anilides, in benzene, except the *p*-nitro anilide exhibited one intense band and an inflexion on the lower frequency side (figure 1). The *p*-nitro anilide however exhibited two distinct C=O bands. All the anilides exhibited only one C=C band each.

The solvents affected the pattern of the C=O bands significantly. The inflexions observed on the carbonyl bands in benzene disappeared in other solvents viz. CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN. Of the two well-resolved C=O bands of *p*-nitroanilide, the higher frequency band increased in intensity with increase in the polarity of the solvent and it is the only band observed in CH<sub>3</sub>CN.

The splitting of the C=O bands may be due to Fermi resonance or to the presence of two conformers. The former is ruled out since no splitting was observed in solid state spectra (KBr pellets). The split in the carbonyl bands was therefore attributed

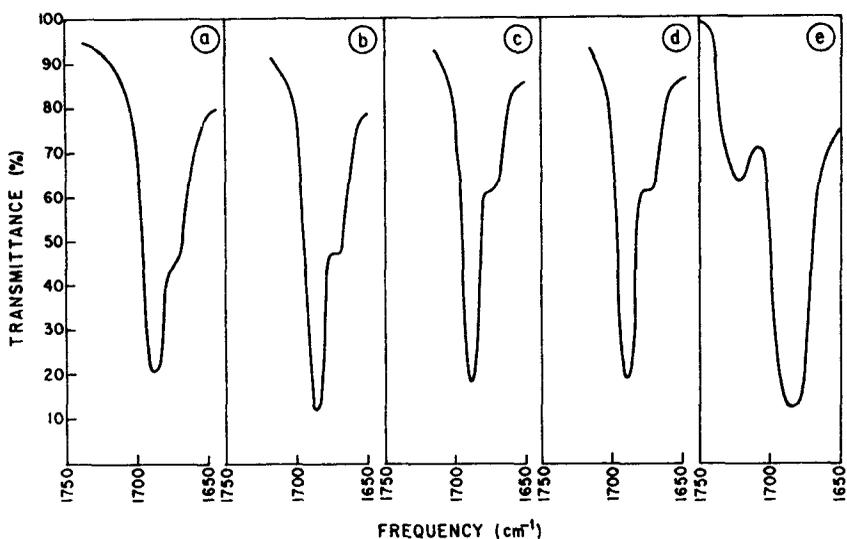
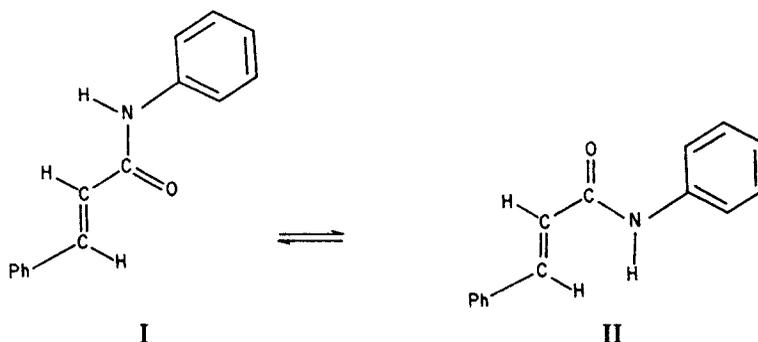


Figure 1. The C=O bands of cinnamanilides in C<sub>6</sub>H<sub>6</sub> (a) *p*-OCH<sub>3</sub> (b) *p*-CH<sub>3</sub> (c) *p*-H (d) *p*-Br and (e) *p*-NO<sub>2</sub>.

to the coexistence of two conformers viz. *s-cis*(I) and *s-trans*(II) in the equilibrium.



On analogy with the band assignments of  $\alpha, \beta$ -unsaturated ketones, the higher frequency bands were assigned to the *s-cis* form in which the field effect of the C=C bond increases the C=O frequency (Erskine and Waight 1960). The lower frequency inflexions/bands, were assigned to the *s-trans* form where the C=C group lowers the C=O frequency by the conjugative effect.

In benzene solution, as each compound consists of a mixture of two conformers, two C=C bands corresponding to the two conformers are expected as in the case of C=O bands. But the spectra of each of the anilides exhibited only one band. The absence of the second band may be due either to very small frequency difference between the two C=C bands which probably did not permit resolution or very low intensity of the *s-trans* band. The low intensity of the *s-trans* C=C bands may be easily understood as they are expected to be nearly 1/6th of the intensity of the C=O (*s-trans*) bands i.e. inflexions in these cases (Erskine and Waight 1960). The inflexions observed, as is evident from the spectra, are very weak (figure 1). The C=C band observed may, therefore, be largely due to the *s-cis* form.

The assignments of the bands received support from the frequency separations and intensity ratios of the bands corresponding to the different conformers. The separation between the higher frequency carbonyl bands and the C=C bands are in the range 52–94  $\text{cm}^{-1}$  which is the range generally found for *s-cisoid* compounds. The intensity ratios of the C=O and C=C bands are of the order 0.26–2.17 (table 1). This is also closer

**Table 1.** The stretching frequencies ( $\text{cm}^{-1}$ ) and intensity ratios of C=O and C=C bands of cinnamanilides in benzene.

Substituent	$\nu_{\text{C=O}}$ ( <i>s-cis</i> )	$\nu_{\text{C=O}}$ ( <i>s-trans</i> )	$\nu_{\text{C=C}}$ ( <i>s-cis</i> )	$\epsilon_{\text{C=O}}$	
				( <i>s-cis</i> )	( <i>s-trans</i> )
OCH <sub>3</sub>	1682	1669*	1630	2.0	1.7
CH <sub>3</sub>	1684	1670*	1630	2.8	1.9
H	1688	1672*	1630	3.8	2.2
Br	1690	1673*	1630	3.8	1.8
NO <sub>2</sub>	1724	1690	1630	0.15	0.3

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to the range normally found for the compounds in *s-cis* conformation (Erskine and Waight 1960).

### 3.1 Effect of substituents on the C=O bands

The frequencies of both the C=O (*s-cis*) and C=O (*s-trans*) bands are affected by the substituents. The electron releasing groups viz. OCH<sub>3</sub> and CH<sub>3</sub> lowered the C=O frequencies while, the electron attracting groups viz. Br and NO<sub>2</sub> enhanced them. A linear relationship was obtained between the C=O frequency and the Hammett  $\sigma$  constants (figure 2). It is interesting to note that the NO<sub>2</sub> group produced an unusually high shift in the C=O frequency.

In anilides the *p*-electrons on the N atom may interact either with the  $\pi$ -electrons of the C=O bond (amide resonance) or with the  $\pi$ -electrons of benzene ring depending on the other groups present in the benzene ring. The electron-releasing OCH<sub>3</sub> and CH<sub>3</sub> groups oppose the interaction of *p*-electrons with the  $\pi$ -electrons of the benzene ring and favour the amide resonance and therefore the frequency of the C=O band is lowered by these groups. Strong electron-attracting groups like NO<sub>2</sub> augment *p*-electron interaction with the benzene ring and suppress the amide resonance. This retards the C=O bond polarisation and enhances its stretching frequency.

### 3.2 Conformations of the molecules and their stabilities

From the relative intensities of the C=O (*s-cis*) and C=O (*s-trans*) bands (figure 1), it appears that the *s-cis* form is predominant in all the anilides except the *p*-nitroanilide in which the *s-trans* form is predominant.

The relative stabilities of the  $\alpha, \beta$ -unsaturated carbonyl compounds were shown to depend on the (1) repulsive electrostatic interactions between the  $\pi$ -electrons of the C=O and C=C bonds in the *s-cis* form and (2) the steric interactions in the *s-trans* form (Erskine and Waight 1960; Noack and Jones 1961; Hayes and Timmons 1968; Bowles *et al* 1969). The cinnamamide and N-methyl cinnamamide were shown to

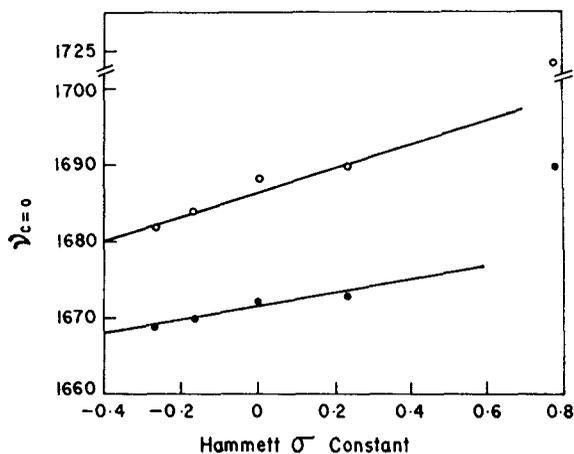
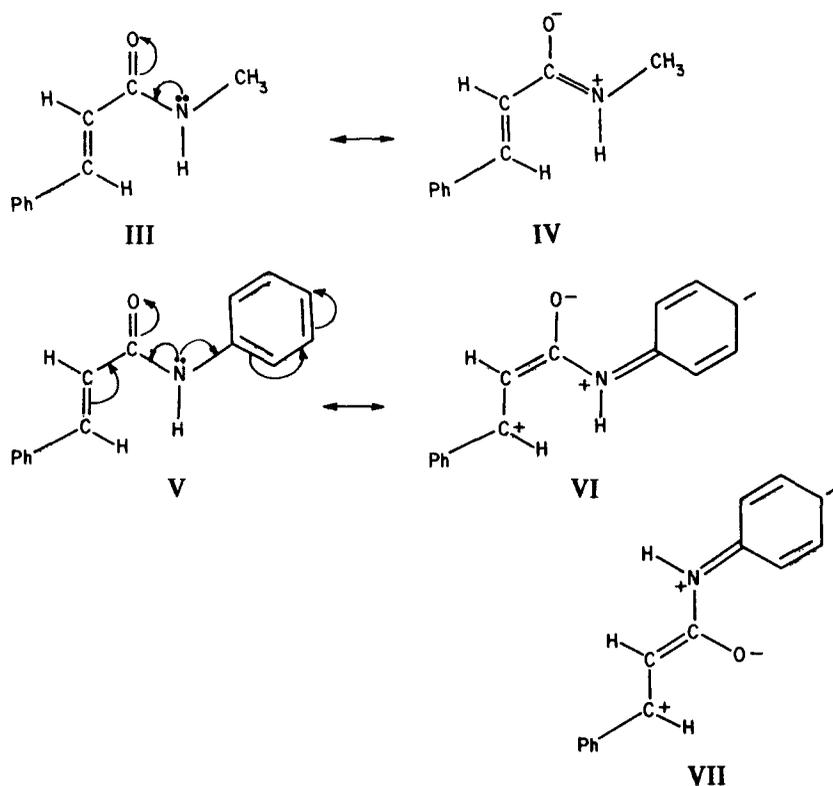


Figure 2. A plot of  $\nu_{C=O}$ -*s-cis* (○) and  $\nu_{C=O}$ -*s-trans* (●) of cinnamanilides vs Hammett  $\sigma$  constants.

exist exclusively in the *s-trans* form (Currie *et al* 1969). This may be due to the predominance of the  $\pi$ -electron repulsions in the *s-cis* form over the steric effect offered by N atom of the amide group in the *s-trans* form. If this is true, the cinnamanilide is also expected to get stabilised in the *s-trans* form as the bulk steric effect due to the N atom in the *s-trans* form remaining the same, the  $\pi$ -electron repulsions in cinnamanilide are greater than those in N-methyl cinnamamide. This is due to increased  $\pi$ -electron density in the C=O bond whose polarisation is retarded by the interaction of the *p*-electrons of the N atom with the benzene ring.

It may be the greater repulsive interaction between the anilide nitrogen atom and the  $\beta$ -carbon. The N atom of the cinnamanilide acquires considerable positive charge due the amide resonance or *p*-electron interaction with the benzene ring (V). The resonance in the enone system makes the  $\beta$ -carbon positive (VI). The positive nitrogen and  $\beta$ -carbon atom are sufficiently close in the *s-trans* form for the electrostatic repulsion to be significant enough to destabilise it (VI). The *s-cis* form (VII) is therefore more stable.



A similar explanation was earlier offered for explaining the exclusive stability of the *s-cis* form of phenyl cinnamate (Venkateswarlu and Subrahmanyam 1988).

The substituents in the anilide ring are found to affect the *s-cis/s-trans* ratio significantly. The electron-releasing groups viz.  $\text{OCH}_3$  and  $\text{CH}_3$  lowered the ratio compared to that in cinnamanilide indicating that they stabilise the *s-trans* form. The decrease in the *s-cis/s-trans* ratio may not be due to the increase in the  $\pi$ -electron

repulsions because the electron-releasing groups increase the C=O bond polarisation. Consequently the  $\pi$ -electron density of the C=O bond and thus the electrostatic repulsions of the C=O and C=C bonds decrease. Hence it may be due to decrease in the electrostatic repulsions between the N and  $\beta$ -carbon. The electron-releasing groups oppose the interaction of  $p$ -electrons of N atom with the benzene ring and thereby reduce the positive charge on the N atom. The bromo substituent has little effect on the *s-cis/s-trans* ratio.

The electron attracting nitro group however largely decreased the *s-cis/s-trans* ratio. The stabilisation of the *s-trans* form may be due to the predominance of  $\pi$ -electron repulsions in the *s-cis* form over the electrostatic repulsions in the *s-trans* form. The nitro group augments the interaction of the  $p$ -electrons of N with benzene ring and this retards the C=O bond polarisation and retains greater  $\pi$ -electron density in the C=O bond resulting in the increase in the repulsions between the  $\pi$ -electrons of the C=O and C=C bonds.

The results of the present investigation suggest that the relative stabilities of the *s-cis* and *s-trans* forms are determined not only by the  $\pi$ -electron repulsions between C=O and C=C bonds in the *s-cis*, but also on the electrostatic repulsions between the anilide N atom and the  $\beta$ -carbon atom in the *s-trans* forms.

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