# Infrared Spectra of Substituted Chalcones and Some of Their Ferrocene Analogues

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The infrared spectra of substituted chalcones and some of their ferrocene analogues were measured in the region of fundamental and first overtone C=O stretching bands. The formation of hydrogen bonds between the substituted chalcones and phenol was examined in the O-H stretching region.

The frequencies of fundamental and first overtone C=O stretching bands for *s*-*cis* and *s*-*trans* conformers and also  $\Delta\nu(OH)$  values were found to be linear dependent upon  $\sigma$ -constants of substituents in a series of 3- and 4-substituted and 3'- and 4'-substituted chalcones. Linear correlations between the C=O stretching frequencies and  $\sigma$ -constants were found also in two series of substituted ferrocene analogues of chalcones.

Bearing the obtained results in mind a transfer of the substituent effect through the double bond, through the bonding system in *s*-*cis* and *s*-*trans* conformations and the effect of a ferrocenyl residue on this transfer is discussed.

Our previous papers [1, 2] dealt with the study of relative basicity and infrared spectra of ferrocene analogues of chalcones. Cukerman and co-workers [3] reported infrared spectra of 4- and 4'-substituted chalcones and found — basing upon seven values — a linear correlation between the C=O stretching frequencies and  $\sigma$ -constants of substituents for s-cis conformers of 4-substituted chalcones: this relationship was, however, not statistically evaluated. In a series of 4'-substituted chalcones the C=O stretching frequencies of no more but five derivatives were reported. The above-mentioned authors determined further the integrated intensities of C=O stretching bands of substituted chalcones [4], investigated hydrogen bonds with phenol in a series of 4- and 4'-substituted chalcones [5] and found the linear correlation of seven and six  $\Delta \nu$ (OH) values with  $\sigma$ -constants, respectively.

There is no doubt that these papers are of great value as far as the examination of chalcones is concerned, nonetheless they are based upon relatively small number of experimental data when studying semi-empirical relationships.

This paper which extends our previous studies, deals with the interpretation of infrared spectra of a greater number of substituted chalcones  $XC_6H_4CH = CHCOC_6H_5$ (I) and  $C_6H_5CH = CHCOC_6H_4X$  (II), as well as with some ferrocene analogues of chalcones  $C_5H_5FeC_5H_4CH = CHCOC_6H_4X$  (III) and  $XC_6H_4CH = CHCOC_5H_4FeC_5H_4COC_6H_5$  (IV), where X stands for substituents in position 3- or 4- at the benzene ring. In the case (IV) the substituent  $-COC_6H_5$  is attached to the position 1'- of the ferrocene skeleton. We tried to get semi-empirical relationships from the spectral data to evaluate them statistically and to compare them mutually.

### Experimental

The preparation, purification, melting points and analytical data of substances under study were reported earlier [1, 6, 7]. Infrared spectra were measured with a double-beam UR-20 spectrophotometer (Zeiss, Jena) in the 1500-1800 and 3100-3700 cm<sup>-1</sup> region. The wave-number scale was calibrated using the spectrum of an indene, camphor and cyclohexanone mixture [8] and also the spectrum of 1,2,4-trichlorobenzene.

For C=O stretching frequency measurement the  $10^{-2}$  M solutions of chalcones (I) and (II) in carbon tetrachloride in 0.1 cm cells were employed. The first overtone bands of substances (I) and (II) were taken at a  $3 \times 10^{-2}$  M concentration in carbon tetrachloride in 5 cm cells.

Ferrocene analogues of chalcones (III) and (IV) were measured in  $2 \times 10^{-3}$  M and  $4 \times 10^{-3}$  M concentrations in 0.5 and 0.25 cm cells, respectively, dissolved in carbon tetrachloride. Frequency readings due to fundamental and overtone C=O stretching bands were accurate to  $\pm 1$  cm<sup>-1</sup> excepting the first overtone bands of *s*-trans conformers where the reading error was within  $\pm 3$  cm<sup>-1</sup>.

The spectra of phenol forming hydrogen bonds with chalcones (I) and (II) were measured at  $10^{-1}$  M concentration of chalcone,  $2 \times 10^{-2}$  M concentration of phenol in a 0.25 cm cell carbon tetrachloride being the solvent.

The frequency readings of the broad absorption bands of the bonded O-H group were accurate to  $\pm$  3 cm<sup>-1</sup>.

Carbon tetrachloride, anal. grade (Lachema) was used for all measurements. For linear correlations the  $\sigma$ -constants of substituents reported by *McDaniel* and *Brown* [9] were applied. Parameters of linear correlations were calculated from the non approximated statistical relations,[10] with a Gier digital computer.

## **Results and Discussion**

As it is known from the preceding papers [3, 11], chalcones of type (I) and (II) exist in an equilibrium mixture of two conformers: *s*-trans and *s*-cis when dissolved in organic solvents. Both these conformers exhibit two absorption bands in the C=O stretching vibrations region. The band at the lower frequency was assigned to the C=O stretching mode of *s*-trans conformer whereas that at the higher frequency to the C=O stretching mode of *s*-cis conformer. The measured C=O stretching frequencies of substituted chalcones (I) and (II) are listed in Tables 1 and 2.

To enable comparison, the values reported by *Cukerman* and co-workers [3-5] are also given in Tables 1 and 2.

In attempting to correlate results obtained by us with  $\sigma$ -constants of substituents, from eleven experimental points, the correlations for chalcones (I) were found as follows (Fig. 1):

$$\nu(C=O) \ s\text{-trans} = 11.26(\pm \ 0.84)\sigma + 1652.2(\pm \ 0.0), \qquad (1)$$
  
$$s = + \ 1.30 \qquad r = 0.976$$

$$\nu(C=O) \ s-cis = 8.76(\pm 0.88)\sigma + 1672.2(\pm 0.0). \tag{2}$$
  
$$s = + 1.36 \ r = 0.957$$

(s = standard deviation, r = correlation coefficient.)

## Table 1

No.	X	$\nu(C=0)$ s-trans		v(C=O) s-cis		$2\nu(C=O) 2\nu(C=O)$		⊿r(OH)	
		a	b	a	ь	s-trans a	a a	a	b
1	4-N(CH <sub>3</sub> ) <sub>2</sub>	1642	1641	1663	1663	3233	3315	250	246
2	4-NH <sub>2</sub>	1645	_	1667	_		3322		_
3	$4 - OCH_3$	1648	1644	1670	1667	3247	3327	223	223
4	4-CH <sub>3</sub>	1652	1649	1672	1669	3249	3330	214	210
5	3,4-O <sub>2</sub> CH <sub>2</sub> -	1649	—	1670		3244	3328	215	
6	$4 - C_6 H_5$		1648		1670				201
7	н	1653	1650	1672	1671	3248	3329	205	206
8	4-F	1655	1652	1675	1673	3252	3335	203	_
9	4-Cl	1655	1652	1675	1675	3253	3334	199	197
10	4-Br	_	1650	_	2			_	_
11	3-Cl	1657		1676		3254	3336	194	
12	4-CN	1658		1676		3255	3338	152	
13	3-NO2	1660		1678	_	3255	3340	160	_
14	$4-NO_2$	-	1647	—	1668	-			158

Infrared spectral data of substituted chalcones (I)

The  $\nu(C=O)$ ,  $2\nu(C=O)$  and  $\Delta\nu(OH)$  values are given in cm<sup>-1</sup>.

a) Values found in this paper.

b) Values given in papers [3-5].

3,4-Dioxymethylenechalcone (substance 5) is also listed, although the general formula (I) does not apply to this substance.

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Infrared spectral data of substituted chalcones (II)

No.	x	$\nu(C=O)$ s-trans		v(C=O) s-cis		$2\nu(C=O) 2\nu(C=O)$	⊿v(OH)		
		a	ь	a	b	s-trans a	a a	a	b
15	4-N(CH <sub>3</sub> ) <sub>2</sub>	1643	1641	1661	1662	3249	3314	264	
16	4-OCH <sub>3</sub>	1649	1644	1668	1666	3239	3324	232	226
17	4-CH <sub>3</sub>	1652	1649	1670	1668	3240	3328	217	215
18	$4-C_6H_5$		1648	_	1668	_			213
19	4-F	1654		1673		3259	3332	200	
20	3-OCH <sub>3</sub>	1655	-	1671		3257	3329	206	
21	4-Cl	1655	1652	1672	1672	3235	3328	193	190
22	4-Br	1655	1652	1671	1673	3233	3329	194	_
23	3-Cl	1656	_	1674		3242	3334	184	
24	3-Br	1656	-	· 1674	_	3235	3333	185	_
25	3-NO2	1659		1677	_	3253	3339	167	
26	$4 - NO_2$	1660	1653	1676	1675	3251	3337	162	154

The  $\nu(C=O)$ ,  $2\nu(C=O)$  and  $\Delta\nu(OH)$  values are given in cm<sup>-1</sup>.

a) Values found in this paper.

b) Values given in papers [3-5].



Fig. 1. Relationship between  $\nu$ (C=O) and  $\sigma$  for chalcones (I). • *s*-cis conformers;  $\bigcirc$  *s*-trans conformers.

When evaluating the statistical significance of both correlations it is obvious that the correlation (1) is statistically significant adopting the 1 per cent level for tests and for correlation (2) the 5 per cent level of significance. On the other hand, the parameters of a linear correlation led, if figured out from seven experimental points as obtained by *Cukerman* and co-workers [3], to following results:

$$\nu(C=0) \ s-cis = 11.08(\pm 1.36)\sigma + 1671.3(\pm 0.5).$$
(3)  
$$s = \pm 1.15 \qquad r = 0.964$$

The mentioned relationship is statistically significant adopting the 10 per cent level of significance for tests. The relationship (2) obtained by us is, when compared with that of (3) statistically more significant, this being evidenced — besides the numerical value of the level of significance — by the lower per cent value of the error of the slope, or by other words 10% towards 12%. From the mentioned fact follows that it is possible to correlate also the C=O stretching frequencies of *s*-trans conformers of substituted chalcones with  $\sigma$ -constants of substituents. It is worth noting that Dimmock and co-workers [12] already correlated the C=O stretching frequencies of *s*-cis and *s*-trans conformers of compounds C<sub>4</sub>H<sub>9</sub>COCH = CHC<sub>6</sub>H<sub>3</sub>X<sub>1</sub>X<sub>2</sub> with  $\sigma$ - and  $\sigma$ \*-constants.

We found even both conformers of chalcones (II) to afford linear relationships between the C=O stretching frequencies and  $\sigma$ -constants of substituents. Of twelve experimental points the dependences were established as being (Fig. 2):

$$\begin{aligned} \nu(\text{C=O}) \ s\text{-trans} &= 10.15(\pm \ 0.57)\sigma + 1652.5(\pm \ 0.3), \\ s &= \pm \ 0.83 \qquad r = 0.984 \end{aligned}$$

$$\nu(C=O) \ s-cis = 9.12(\pm \ 0.89)\sigma + 1670.4(\pm \ 0.4) \,. \tag{5}$$
  
$$s = \pm \ 1.29 \qquad r = 0.956$$



Fig. 2. Relationship between  $\nu(C=0)$  and  $\sigma$  for chalcones (II). • s-cis conformers;  $\bigcirc$  s-trans conformers.

The dependence (4) is statistically significant adopting the 0.1 per cent level and relation (5) the 5 per cent level of significance for tests.

Comparison of the C=O stretching frequencies for *s*-trans conformers as reported in [3, 4] with those given in this paper shows the values in [3, 4] to be mostly lower and they afford unfavourable presumptions for obtaining linear relationships from  $\sigma$ -constants. By a simple reading of the *s*-trans conformer band position, which frequently forms only a shoulder on the higher frequency band it is possible. we believe, to commit a relatively higher error. In this paper, the reading of such absorption bands was done after graphic resolution of the complex band similar to that described by *Hayes* and *Timmons* [11].

A distinctly separated first overtone C=O stretching band of *s*-*cis* conformer could be seen at about 3330 cm<sup>-1</sup> in carbon tetrachloride at an appropriate concentration of the chalcone used. The first overtone C=O stretching band of the *s*-trans conformer appears at about 3250 cm<sup>-1</sup> as a little pronounced shoulder on the first overtone C=C stretching band.

The first overtone C=O stretching frequencies of *s*-*cis* conformers (Tables 1 and 2) can be satisfactorily correlated with  $\sigma$ -constants of substituents of both types of chalcones under study (Fig. 3).

For chalcones (I):

$$2\nu(C=0) \ s - cis = 14.55(\pm 1.32)\sigma + 3330.4(\pm 0.0).$$
(6)  
$$s = + 2.04 \qquad r = 0.965$$

For chalcones (II):

$$2\nu(C=0) \ s-cis = 14.11(\pm 1.44)\sigma + 3327.8(\pm 0.7).$$
(7)  
$$s = + 2.09 \ r = 0.952$$



Fig. 3. Relationship between  $2\nu(C=O)$  and  $\sigma$  for s-cis conformers of chalcones. • chalcones (I);  $\bigcirc$  chalcones (II).

Relationships (6) and (7) are statistically significant adopting the 2 and 5 per cent level of significance for tests, respectively. The C=O stretching frequencies for *s*-trans conformers of ferrocene analogues of chalcones (III) which also exist in solutions as an equilibrium mixture of both conformers [2] are listed in Table 3.

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Infrared spectral data of substituted ferrocene analogues of chalcones (III)

No.	х	v(C=O) s-trans	v(C=O) s-cisc
27	4-N(CH <sub>2</sub> ),	1633	1657.0
28	4-OCH <sub>3</sub>	1637	1660.5
29	4-CH <sub>3</sub>	1638	1662.5
30	н	1640	1665.5
31	4-F	1641	1664.5
32	3-OCH <sub>3</sub>	1639	1662.0
33	4-Cl	1642	1663.5
34	4-Br	1643	1663.0
35	3-Cl	1643	1664.5
36	3-Br	1643	1665.0
37	4-CN	1645	1664.5
38	3-NO <sub>2</sub>	1645	1666.0
39	4-NO,	1646	1666.5

The  $\nu(C=O)$  values are given in cm<sup>-1</sup>.

c) Values reported in previous paper [2].

-0.8

The measured values can be well correlated with the  $\sigma$ -constants of substituents. For thirteen experimental points results shown were obtained (Fig. 4):

0.4

0.8 0

Fig. 4. Relationship between v(C=O) and  $\sigma$  for s-trans conformers of ferrocene analogues of chalcones (III).

0

-0.4

The relationship is statistically significant adopting the 0.1 per cent level of significance for tests.

Ferrocene analogues of chalcones (IV) behave in solvents like compounds  $C_5H_5FeC_5H_4COH = CHC_6H_4X$  [2]. In carbon tetrachloride, they exist in form of a single conformer, which, apart from the C=O band of benzoyl group at 1656 –

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Infrared spectral data of substituted ferrocene analogues of chalcones (IV)

No.	X	$\nu(C=O)$
40	4-N(CH <sub>3</sub> ) <sub>2</sub>	1656
41	4-NH <sub>2</sub>	1659
42	4-OCH <sub>3</sub>	1661
43	4-CH <sub>3</sub>	1662
44	н	1665
45	4-F	1665
46	4-Cl	1666
47	4-CN	1667
48	3-NO2	1668
49	$4-NO_2$	1669

The  $\nu(C=O)$  values are given in cm<sup>-1</sup>.

 $-1669 \text{ cm}^{-1}$ , exhibit only one unsplit absorption band attributable to the C=O stretching vibration of a chalcone grouping (Table 4). The measured C=O stretching

frequencies can be correlated for ten experimental values with  $\sigma$ -constants of substituents as follows (Fig. 5):

$$\nu(C=O) = 7.28(\pm 0.62)\sigma + 1663.4(\pm 0.1).$$
(9)  
$$s = + 1.05 \qquad r = 0.972$$



Fig. 5. Relationship between  $\nu(C=0)$  and  $\sigma$  for ferrocene analogues of chalcones (IV).

The relationship is statistically significant 2 per cent significance level being adopted for tests.

Under conditions given in the experimental part for chalcones (I) and (II) the differencies between the frequencies of free and bonded OH group of phenol under formation of >C=0...H-O-type hydrogen bonds (Table 1) were recorded.

The  $\Delta \nu$ (OH) values correlate well with the  $\sigma$ -constants of substituents (Figs. 6 and 7) giving following results:

For chalcones (I) based upon eleven experimental points:

$$\begin{aligned}
4\nu(\text{OH}) &= -56.51(\pm 3.35)\sigma + 205.6(\pm 0.7). \\
s &= \pm 4.83 \qquad r = -0.984
\end{aligned}$$
(10)



Fig. 6. Relationship between  $\Delta v(OH)$  and  $\sigma$  for chalcones (I).



Fig. 7. Relationship between  $\Delta \nu$ (OH) and  $\sigma$  for chalcones (II).

For chalcones (II) based upon thirteen experimental points:

$$\begin{aligned} \Delta\nu(\text{OH}) &= -63.32(\pm 2.42)\sigma + 209.5(\pm 1.1) \,. \\ s &= \pm 3.54 \qquad r = -0.992 \end{aligned} \tag{11}$$

The  $\Delta \nu(OH)$  values of compounds 6, 14 and 18 from paper [5] were also implied into the above-mentioned linear correlations. Both dependence (10) and (11) are statistically significant the 0.1 per cent significance level being adopted.

If the statistical parameters of the same dependences are calculated using the  $\Delta v(OH)$  values as reported in [5] following results are obtained:

For chalcones (I) from seven experimental points:

$$\Delta \nu(\text{OH}) = -54.08(\pm 3.69)\sigma + 203.8(\pm 0.4).$$

$$s = \pm 4.43 \qquad r = -0.989$$

$$(12)$$

For chalcones (II) from six experimental points:

$$\Delta \nu(\text{OH}) = -67.87(\pm 3.94)\sigma + 207.0(\pm 0.9).$$
(13)  
$$s = \pm 3.33 \qquad r = -0.993$$

Relationships (12) and (13) are statistically significant the 1 per cent significance level being adopted. As seen, relationships (10) and (11) obtained in this paper are statistically more significant due to the greater number of experimental data used than relationships (12) and (13) employing values reported in [5].

When comparing the slope values of all linear relationships between the C=O stretching frequencies and  $\sigma$ -constants of *s*-trans conformers with those of *s*-cis conformers, one finds out that they are always higher with *s*-trans conformers. The mentioned fact suggests that the substituent effect from benzene ring is being transferred to the carbonyl group easier with *s*-trans than with *s*-cis conformation of the chalcone molecule. If the ratios of the slope of linear dependences for both conformers are expressed by the coefficient  $\eta = \varrho(s - cis)/\varrho(s - trans)$  following values are found in particular systems: for chalcones (I)  $\eta = 0.78$ , for chalcones (II)  $\eta = 0.90$  and for ferrocene analogues (III)  $\eta = 0.67$ .

This coefficient can be calculated by analogy from the slopes of linear relationships between the C=O stretching frequencies and  $\tau$  for compounds  $X_1X_2C_6H_3CH =$ = CHCOC<sub>4</sub>H<sub>9</sub> described by *Dimmock* and co-workers [12]. The value of this coefficient 0.76 is in good agreement with the  $\eta$ -value obtained by us for chalcones (I). In both types of molecules a transfer of the substituent effect through the same system, *i.e.* from benzene ring through the double bond to the carbonyl group is involved.

A different situation has been found with chalcones (II), where the substituent effect is transferred from the benzene ring to the carbonyl group directly. The higher value  $\eta = 0.90$  evidences the smaller difference between the slopes of two various conformers; consequently, the conformation itself influences the transfer of the substituent effect to a small extent only. Bearing this in mind it is rather difficult to rationalize the low value of the coefficient  $\eta$  for ferrocene analogues (III), this value would be expected to be comparable with that of chalcones (II). We assume therefore, that the explanation should lie in the extraordinary strong electron--donating effect associated with the ferrocenyl residue which results in a different transfer of the electronic effect with two various conformers. When comparing the slopes of the relationships between the C=O stretching frequencies and  $\sigma$  of ferrocene analogues of chalcones (III) with those of chalcones (II) it becomes evident that both conformers reveal lower values with ferrocene analogues of chalcones (III). Ferrocenyl residue retards the transfer of the substituent effect from the benzene ring to the carbonyl group in both conformations, this being the consequence of a strong electron-donating character of ferrocenyl grouping. Ferrocenyl group increases the electron density at the carbon atom of the C=0 group thereby lowering its sensitivity towards the electron effects of substituents. By comparison of the numerical values of these slopes one can see that the retardation of the transfer of the substituent effect, due to the ferrocenyl group is more favoured with s-cis conformations. The value of the slope of the linear dependence of the C=0 stretching frequencies upon  $\sigma$  with compounds (IV) ( $\rho = 7.28$ ) is greater than that of analogous derivatives  $C_5H_5FeC_5H_4COCH = CHC_6H_4X$  ( $\rho = 4.26$ ) [2].

This can be explained by assuming that the benzoyl group present in compounds (IV) lowers the electron-donating effect of the ferrocenyl residue on the second C=O group, thereby facilitating the transfer of the substituent effect in the system in question.

An analogous effect of the benzoyl group in substances (IV) was observed when investigating hydrogen bonds with phenol [1]. The slopes of relationships between C=O stretching frequencies and  $\sigma$  of chalcones (I) and (II) make it possible to calculate the transfer coefficient of the substituent effect through the double bond:

$$\tau = \varrho(I)/\varrho(II).$$

For s-trans conformers the calculated value  $\tau = 0.96(\pm 0.31)$  and for s-cis conformers  $\tau = 1.09(\pm 0.14)$ .

Bearing in mind the error while determining both values close to each other, one can say that the average value of the coefficient obtained by us approaches one. The value of the transfer coefficient for substituted chalcones calculated by *Cukerman* and co-workers [5] from the slopes of relationships (12) and (13)  $\tau = 0.79(\pm 0.10)$ . Value of this coefficient calculated by us from the slopes of relationships (10) and (11) was found to be a little higher, *i.e.*  $\tau = 0.89(\pm 0.09)$ . Values obtained from relationships between C=O stretching frequencies and  $\sigma$  are always higher than  $\tau$ values calculated from relationships between  $\Delta \nu(OH)$  and  $\sigma$  in spite of the fact that the values thus calculated are bearing a relatively great error. This fact can be explained by assuming that the distribution of the  $\pi$ -electron cloud is altered along the whole conjugated system as a result of a hydrogen bond formation between the chalcone and phenol; consequently, the ability of the double bond to transfer electron effects of substituents is lowered.

The slopes of relationships between first overtone C=O stretching frequencies and  $\sigma$  were found to be always higher when compared with those of the fundamental C=O stretching frequencies and  $\sigma$  of the *s*-cis conformers of both chalcones (I) and (II). This can be attributed to the anharmonic effect associated with the formation of first overtone C=O stretching frequencies. The measured first overtone frequencies of chalcones (I) and (II) are by 8-16 cm<sup>-1</sup> lower than values calculated from the fundamental frequencies. Using the relationship between first overtone C=O stretching frequencies and  $\sigma$  to establish the transfer coefficient through the double bond  $\tau$  a value close to one has been determined.

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