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# Electronic Spectra of Ferrocenyl Chalcones:

## On the Substituent Dependence of the $\lambda_{max}$ of the d − d Transition

**Štefan Tomá**[a,*], **Anton Gáplovský**[b], and **Ivan Pavlík**[c]

[a] Department of Organic Chemistry, and [b] Institute of Chemistry, Comenius University, CS-842 15 Bratislava, Czechoslovakia

[c] Department of Inorganic Chemistry, Technical University, CS-530 00 Pardubice, Czechoslovakia

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The electronic absorption spectra of two series of ferrocenyl chalcones (*Fc* − CH = CH − CO − *Ar*, **1** and *Fc* − CO − CH = CH − *Ar*, **2**) in methanol and *n*-hexane were recorded. Excellent correlations of $\lambda_{max}$ of the d–d transition between 450–540 nm with *Hammett* substituent constants were found in **1**, and reasonable correlations in **2**. In methanol a bathochromic shift of this band occurs. An explanation of this phenomenon, partially based on ligand field calculations, is presented.

*(Keywords: Ferrocene analogues of chalcones; Hammett correlation, Metallocenes)*

*Elektronenabsorptions-Spektren von Ferrocenylchalkonen. Zur Substituentenabhängigkeit von $\lambda_{max}$ des d − d-Überganges*

Die Elektronenabsorptions-Spektren von zwei Reihen von Ferrocenylchalkonen (*Fc* − CH = CH − CO − *Ar*, **1** und *Fc* − CO − CH = CH − *Ar*, **2**) wurden in Methanol und *n*-Hexan gemessen. Für **1** wurde eine ausgezeichnete Übereinstimmung der $\lambda_{max}$-Werte des d − d-Überganges (zwischen 450 und 540 nm) mit den *Hammett*-Substituentenkonstanten gefunden, während sie in der Reihe **2** befriedigend ist. In Methanol erleidet die genannte Bande eine bathochrome Verschiebung.

Eine Erklärung für diese Ergebnisse wird präsentiert, die zum Teil auf Ligandenfeld-Berechnungen basiert.

## Introduction

In the electronic absorption spectra of ferrocene and its simple derivatives two broad low intensity long wave bands located near 325 nm ($\varepsilon$ = 52) and 440 nm ($\varepsilon$ = 91) occur[1]. These bands were assigned to the d – d transition of iron in ferrocene[2–4]. The 440 nm band was found to be moderately substituent dependent[5].

Electron-withdrawing substituents cause bathochromic and electron-donating substituents hypsochromic shifts. The position and intensity of this band is very sensitive to a ring tilt in bridged ferrocenes[6] and may be shifted up to 472 nm ($\varepsilon = 450$) in [2]ferrocenophane[7]. A specific large bathochromic shift (461 nm, $\varepsilon = 272$) due to the interaction between the non-bonding d-orbital of the iron atom and the lone pair of electrons of the sulphur atom was observed very recently[8] in the case of 1,4,7-trithia[7]ferrocenophane.

The electronic spectra of ferrocenyl chalcones were briefly mentioned in Ref.[9]. Four bands have been reported for these compounds[10]: Bands at 410–555 nm and 375–440 nm (sometimes as a shoulder) were assigned to the ferrocene moiety, a 290–310 nm band was ascribed to the whole ligand (K-band) and a 225–270 nm band was assigned to the local carbonyl group transition. So far, however, the substituent dependence of these bands has not been studied. The main goal of our work, was to investigate this dependence in two series of ferrocenyl chalcones, i.e. *Fc* – CH = CH – CO – *Ar* (**1**) and *Fc* – CO – CH = CH – *Ar* (**2**). A second aim of this study was to find whether the position of the 440 nm band was solvent dependent.

## Results and Discussion

From the data presented in Tables 1 and 2 three distinct absorption bands can be found: Bands near 310 nm could be assigned in accord with Ref.[10] as K-bands belonging to $\pi$–$\pi^*$ transitions. An attempt to correlate their $\lambda_{\max}$ with *Hammett* constants (Fig. 1) revealed a similar behaviour as for simple chalcones[14,15] i.e. correlation is divided in two parts:

$$\rho_{\mathrm{I}} = -96.82; \quad r = 0.988; \quad S_\rho = \pm 8.59;$$
$$\rho_{\mathrm{II}} = 13.65; \quad r = 0.934; \quad S_\rho = \pm 2.12.$$

Since the band near 370 nm is not well developed in all chalcones from either series we did not study its substituent dependence. The most pronounced substituent effect was observed for the 440 nm band. Fig. 2 reveals that this transition band is quite different from that observed in ferrocene and ferrocenecarbaldehyde. First of all, the band is shifted by 46 nm to higher wavelength, its intensity is higher and it is "sharper". This allows the more precise determination of $\lambda_{\max}$. Fig. 3 shows that an excellent *Hammett* correlation of $\lambda_{\max}$ exists for the spectra in methanol: $\rho = 22.48$; $r = 0.965$; $S_\rho = \pm 1.83$. Correlation of $\lambda_{\max}$ with $\sigma^-$ constants gave $\rho = 19{,}64$; $r = 0.995$; $S_\rho = \pm 0.34$.

An analogus correlation for the spectra in *n*-hexane gave less good results: $\rho = 22.49$; $r = 0.891$; $S_\rho = \pm 3.45$.

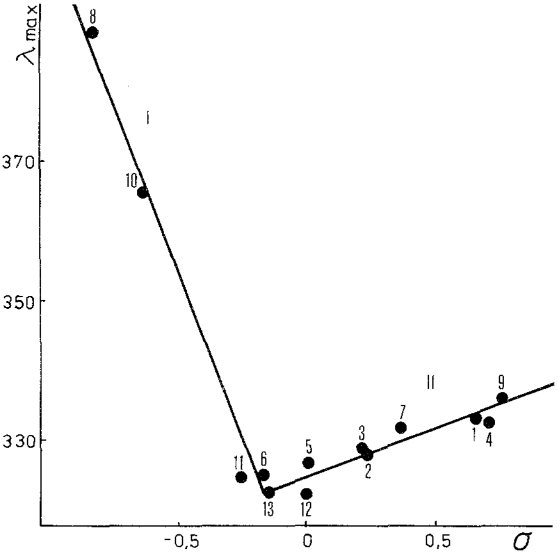

Fig. 1. *Hammett* correlation of the K band (310 nm) of chalcones *Fc*$-$CH$=$CH$-$CO$-$*Ar* with $\sigma$ constants

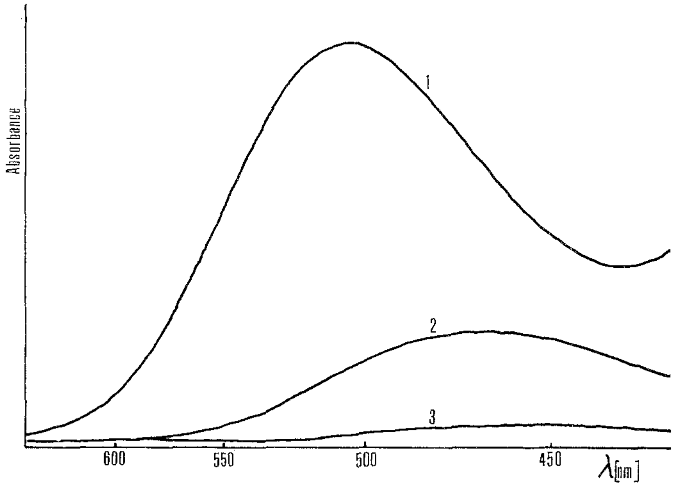

Fig. 2. VIS spectra of *Fc*CH$=$CH$-$CO*Ph* (*1*), *Fc*$-$CHO (*2*), and *Fc*$-$H (*3*); measured in *n*-hexane at $1 \cdot 10^{-3}$ mol/dm$^3$ concentration

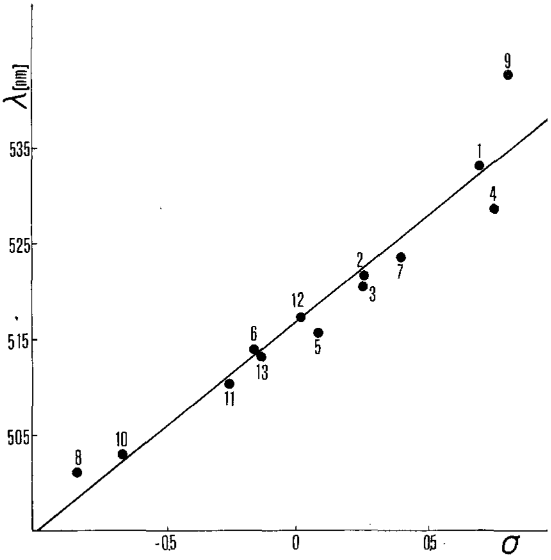

Fig. 3. *Hammett* correlation of $\lambda_{max}$ of the d–d transition bands of chalcones *Fc*CH=CH–CO–*Ar* (in methanol) with σ constants

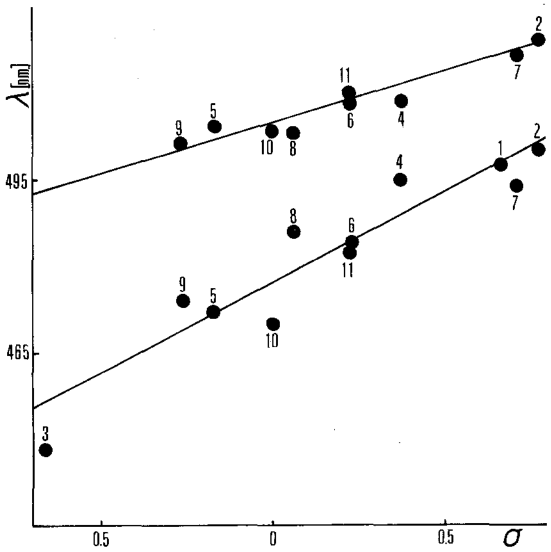

Fig. 4. *Hammett* correlations of $\lambda_{max}$ of the d–d transition bands of chalcones *Fc*COCH=CH–*Ar* in methanol (upper line) and *n*-hexane (lower line) with σ constants

Fig. 4 reveals that a *Hammett* correlation is also possible for series **2** but the agreement is not as good and the $\lambda_{max}$-values for several members of this series are more scattered than in series **1**. For the spectra in methanol the values were $\rho = 15.58$, $r = 0.953$, $S_\rho = \pm 1.88$, and in *n*-hexane $\rho = 32.64$; $r = 0.963$; $S_\rho = \pm 4.06$.

The different behaviour of ferrocenyl chalcones in series **1** and **2** can be explained by assuming that the carbonyl group causes the main perturbation in the whole ligand. The electron withdrawing effect of the carbonyl group modified by the substituted phenyl group is transmitted effectively to the $\beta$-carbon of the double bond i.e. to the end of the conjugated system $-CH=CH-C=O$. This causes a different positive charge at the carbon atom to which the ferrocene moiety is bonded in series **1**, and this charge is stabilized by the iron atom. (The effective stabilization of the positive charge on $C_\alpha$ by the ferrocenyl group is well documented[16,17].). No such a stabilization seems possible in series **2** because here ferrocenyl is not located at the end of the conjugated system. The electron demand of the carbonyl in this case is met mainly by the phenyl group.

The observed solvent dependence of the visible spectra is in accord with the above mentioned hypothesis. A red shift of the d−d band is

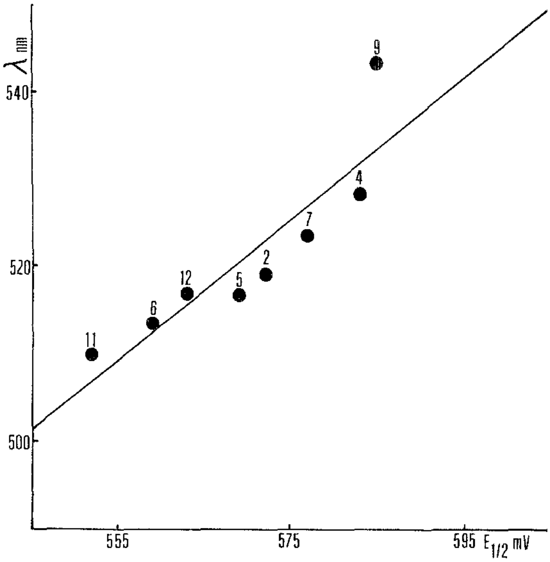

Fig. 5. Correlation of $\lambda_{max}$ of the d−d transition bands of chalcones *Fc*CH=CH−CO*Ar* with the $E_{1/2}$ oxidation potentials of the same compounds taken from Ref.[19]

Table 1. *Electronic spectra of the ferrocenyl chalcones* $Fc-CO-CH=CH-C_6H_4X$ (**2**)

| No. | *X* | $\lambda$(nm) hexane | $\lambda$(nm) methanol | $\lambda$(nm) hexane | $\lambda$(nm) methanol | $\sigma$ | $E_{1/2}$(mV)[19] |
|---|---|---|---|---|---|---|---|
| 1 | $p$-CN | 301.0 | 319.8 | 498.0 | 501.2 | 0.666 | 698 |
| 2 | $p$-$NO_2$ | 302.0 | 333.2 | 500.0 | 518.5 | 0.778 | 698 |
| 3 | $p$-$NH_2$ | 268.8 | – | 447.5 | – | 0.66 | – |
| 4 | $m$-Cl | 293.0 | 313.0 | 495.0 | 507.9 | 0.373 | 690 |
| 5 | $p$-$CH_3$ | 301.8 | 322.0 | 472.7 | 504.1 | −0.170 | 676 |
| 6 | $p$-Br | 300.0 | 318.5 | 484.0 | 509.0 | 0.232 | 689 |
| 7 | $m$-$NO_2$ | – | – | 494.0 | 515.5 | 0.710 | 700 |
| 8 | $p$-F | 294.0 | 317.4 | 487.4 | 503.1 | 0.062 | 684 |
| 9 | $p$-$OCH_3$ | 319.5 | 339.7 | 474.0 | 501.1 | −0.268 | 664 |
| 10 | H | 293.7 | 307.3 | 470.0 | 503.6 | 0.000 | 686 |
| 11 | $p$-Cl | – | – | 483.0 | 510.0 | 0.227 | 689 |

Table 2. *Electronic spectra of ferrocenyl chalcones* $Fc-CH=CH-CO-C_6H_4X$ (**1**)

| No. | *X* | $\lambda$(nm) hexane | $\lambda$(nm) methanol | $\lambda$(nm) hexane | $\lambda$(nm) methanol | $\sigma$ | $\sigma^-$ | $E_{1/2}$(mV)[19] |
|---|---|---|---|---|---|---|---|---|
| 1 | $p$-CN | 312.0 | 333.0 | 505.0 | 532.8 | 0.666 | 0.90 | 472 |
| 2 | $p$-Br | 318.0 | 328.0 | 492.2 | 521.3 | 0.232 | – | 572 |
| 3 | $p$-Cl | 318.0 | 328.7 | 490.0 | 520.5 | 0.227 | – | – |
| 4 | $m$-$NO_2$ | 324.0 | 332.8 | 504.0 | 528.4 | 0.710 | – | 583 |
| 5 | $p$-F | 314.0 | 326.8 | 492.4 | 515.5 | 0.062 | – | 569 |
| 6 | $p$-$CH_3$ | 312.8 | 325.0 | 483.0 | 513.6 | −0.170 | – | 559 |
| 7 | $m$-Cl | 319.4 | 331.7 | 486.9 | 523.7 | 0.373 | – | 577 |
| 8 | $p$-$N(CH_3)_2$ | 349.0 | 388.9 | 470.9 | 501.1 | −0.830 | – | – |
| 9 | $p$-$NO_2$ | 322.0 | 335.9 | 515.0 | 542.5 | 0.778 | 1.24 | 585 |
| 10 | $p$-$NH_2$ | 323.1 | 365.8 | 482.7 | 502.6 | −0.660 | – | – |
| 11 | $p$-$OCH_3$ | 311.0 | 324.5 | 476.5 | 510.0 | −0.268 | – | 552 |
| 12 | H | 310.9 | 321.9 | 486.5 | 516.9 | 0.000 | – | 563 |
| 13 | $p$-$C_2H_5$ | 309.0 | 322.5 | 477.0 | 513.0 | −0.150 | – | – |

observed going from *n*-hexane to methanol. This may be due to the $C=O \cdots HOCH_3$ hydrogen bonding in methanol. A larger red shift was observed after protonation of the carbonyl group by HCl[18].

Ligand field (LF) calculations were carried out as described in Ref.[4] and the results are given in Table 3. The socalled *Rakash* parameter *B* is associated with the interelectronic repulsion of d-electrons. The

Table 3. *Ligand-field parameters of some ferrocene derivatives*

| Compound | Experimental values ($cm^{-1}$) | | | Calculated values ($cm^{-1}$) |
|---|---|---|---|---|
| Ferrocene | $\varepsilon_1 = 22\,800$<br>$\varepsilon_2 = 30\,700$ | $B = 395$<br>$\beta = 0.402$ | $Ds = 4\,837$<br>$Dt = 3\,080$ | $E_{10} = 25\,963$<br>$E_{02} = 3\,948$<br>$(E_{12} = 29\,911)$ |
| *Fc*−CO−CH=CH−*Ph* | $\varepsilon_1 = 21\,053$<br>$\varepsilon_2 = 26\,455$ | $B = 270$<br>$\beta = 0.275$ | $Ds = 4\,087$<br>$Dt = 2\,730$ | $E_{10} = 23\,213$<br>$E_{02} = 2\,698$<br>$(E_{12} = 25\,911)$ |
| *Fc*−CO−CH=CH−*Ph*−$OCH_3$ (*p*) | $\varepsilon_1 = 21\,368$<br>$\varepsilon_2 = 26\,042$ | $B = 234$<br>$\beta = 0.238$ | $Ds = 3\,989$<br>$Dt = 2\,722$ | $E_{10} = 23\,231$<br>$E_{20} = 2\,346$<br>$(E_{12} = 25\,577)$ |
| *Fc*−CO−CH=CH−*Ph*−Br (*p*) | $\varepsilon_1 = 20\,833$<br>$\varepsilon_2 = 26\,178$ | $B = 267$<br>$\beta = 0.272$ | $Ds = 4\,043$<br>$Dt = 2\,702$ | $E_{10} = 22\,977$<br>$E_{02} = 2\,662$<br>$(E_{12} = 25\,639)$ |
| *Fc*−CH=CH−CO−*Ph* | $\varepsilon_1 = 20\,964$<br>$\varepsilon_2 = 26\,178$ | $B = 261$<br>$\beta = 0.266$ | $Ds = 4\,040$<br>$Dt = 2\,709$ | $E_{10} = 23\,050$<br>$E_{02} = 2\,615$<br>$(E_{12} = 25\,665)$ |
| *Fc*−CH=CH−CO−*Ph*−$OCH_3$ (*p*) | $\varepsilon_1 = 21\,097$<br>$\varepsilon_2 = 26\,596$ | $B = 275$<br>$\beta = 0.280$ | $Ds = 4\,114$<br>$Dt = 2\,741$ | $E_{10} = 23\,296$<br>$E_{02} = 2\,751$<br>$(E_{12} = 26\,047)$ |
| *Fc*−CH=CH−CO−*Ph*−Br (*p*) | $\varepsilon_1 = 20\,704$<br>$\varepsilon_2 = 25\,840$ | $B = 257$<br>$\beta = 0.262$ | $Ds = 3\,986$<br>$Dt = 2\,674$ | $E_{10} = 22\,754$<br>$E_{02} = 2\,574$<br>$(E_{12} = 25\,328)$ |

nefelauxetic parameter $\beta$ given by the expression $B_{complex}/B_{ion}$ (for $Fe^{2+}$ ion value $982\,cm^{-1}$ was used) is connected with central-field covalency, and the symmetry-restricted covalency. The lower value of $\beta$ represents the greater Fe − *Cp* covalency. The meaning of $E_{10}$, $E_{02}$ etc. is explained by Fig. 5. The results of LF calculations are in accord with the experimental results. From the comparison of $\beta$-values for ferrocene and ferrocenyl chalcones it follows that there is a higher covalent character of the Fe − *Cp* bond in the chalcones than in ferrocene: *Fc*CH=CHCO*Ph* $\beta = 0.266$; *Fc*COCH=CH*Ph* $\beta = 0.275$ and *Fc*-H $\beta = 0.402$. It is possible to deduce by comparing the $\beta$-values for the parent compounds of both series that the covalent character of the Fe-*Cp* bond is higher in series **1** (i.e. the substituent effects are transmitted better to the iron atom. This is proved also by the change of $\beta$-values in series **1**: $X = OCH_3$, $\beta = 0.280$; $X = H$, $\beta = 0.266$; $X = Br$, $\beta = 0.262$. Nothing like that was observed in series **2**: $X = OCH_3$, $\beta = 0.238$; $X = H$, $\beta = 0.275$; $X = Br$, $\beta = 0.272$.

A further proof that the band near 440 nm corresponds to the d−d transition follows from the linear correlation of the $\lambda_{max}$ with the $E_{1/2}$ oxidation potentials of the corresponding chalcones[19] (Fig. 5). The results of these correlations are $\rho = 0.94$; $r = 0.89$; $s_\rho = \pm 0.2$.

The oxidation potentials of the ferrocene molecule are related to the highest occupied frontier orbital which is mainly d in character.

## Experimental

The ferrocene analogues of chalcones were prepared and purified as described in Refs.[11,12]. The spectra were recorded as $5 \cdot 10^{-4}$ mol/dm$^3$ solutions in *n*-hexane, methanol and hydrogen chloride saturated *n*-hexane on a Perkin-Elmer 450 spectrometer in digital form and the exact values of $\lambda_{max}$ determined to ± 1 nm by the method described in Ref.[13] (see Tables 1 and 2).

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