Monatshefte für Chemie 116, 357—364 (1985)

*Monatshefte für Chemie*
*Chemical Monthly*

# Substituent Dependence of the d-d Transition Band in the Electronic Absorption Spectra of Arylferrocenes and the Corresponding Arylferricenium Salts

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*(Received 4 April 1984. Accepted 27 April 1984)*

The electronic absorption spectra of 22 arylferrocenes and their arylferricenium salts with pentacyanopropenide (*PCNP*) were recorded. The attempted *Hammett* correlation of $\lambda_{max}$ of the d-d transition bands of arylferrocenes revealed that this band is substituent dependent only for strong electron-withdrawing substituents. Excellent correlation of $\lambda_{max}$ of the d-d transition bands with $\sigma^+$ constants was found in the case of arylferricenium cations. Good correlations of $\lambda_{max}$ was also found with the $E_{1/2}$ oxidation potentials measured by cyclic voltametry.

*(Keywords: Hammett correlation; Metallocenes)*

*Substituentenabhängigkeit des d-d-Überganges in den Elektronenabsorptions-Spektren von Arylferrocenen und entsprechenden Arylferricenium-Salzen*

Elektronenabsorptions-Spektren von 22 Arylferrocenen und ihren Arylferricenium-Pentacyanopropenid-Salzen wurden gemessen. Versuchte *Hammett*-Korrelationen des längstwelligen d-d-Überganges ($\lambda_{max}$) zeigten, daß diese Bande nur von stark elektronenanziehende Substituenten abhängig ist. Im Fall der Arylferricenium-Kationen wurde eine ausgezeichnete Korrelation zwischen $\lambda_{max}$ der d-d-Bande und den $\sigma^+$-Konstanten festgestellt. Eine gute Korrelation der $\lambda_{max}$-Werte wurde auch mit den $E_{1/2}$ Oxidationspotentialen gefunden, die durch cyclische Voltametrie meßbar sind.

## Introduction

The long wavelength band near 440 nm in the electronic spectra of ferrocene and its derivatives was assigned to the d-d transition of the iron atom[1–3]. It was found to be moderately substituent dependent[4] and a good correlation of $\lambda_{max}$ of this band with the *Hammett* substituent constants was found for ferrocene analogues of chalcone[5].

Arylferrocenes were the subject of through $^1$H-NMR and $^{13}$C-NMR studies[6,7] as well as electrochemical studies[8,9]. A good correlations of $E_{1/4}$ of the chronopotentiometric oxidation of arylferrocenes with $\sigma_p$ constants was found[8]. The oxidation of arylferrocenes by cyclic voltametry was described only recently[9].

The charge-transfer complex formation of phenylferrocene with *TCNE* was observed with an absorption near 950 nm[10] in nonpolar solvents. The *TCNE* charge-transfer complex of ferrocene was measured in cyclohexane ($\lambda_{max}$ 900 nm and 1 075 nm) and in the solid state ($\lambda_{max}$ 975 nm and 1 150 nm)[11]. In polar solvents *TCNE* causes the oxidation of ferrocene derivatives to the corresponding ferricenium cation radical, which exhibits a band near 620 nm[12]. *TCNE* is reduced under these conditions to the pentacynopropene (*PCNP*) anion which exhibits characteristic absorption bands at 393 nm and 412 nm[13].

The ferricenium cation radical was detected by EPR in acetonitrile solutions of ferrocene and *TCNE*[14]. The crystal structure of $C_{10}H_{10}Fe^{(+)}(NC)_2C=C(CN)O^{(-)}$ was reported recently[15]. The EPR as well as $^{13}$C-NMR spectra of the phenylferricenium cation[16, 17] were measured and it was proved that the unpaired electron is mainly located in a d-orbital of the iron atom[18].

Electronic spectra of arylferrocenes have been reported several times[19–21]. It was proved[20,21] that there is no through resonance *via* the Fe-atom in the case of 1,1′-diarylferrocenes but no systematic investigation on the substituent dependence of the $\lambda_{max}$ of d-d bands was carried out.

The main goal of the work of this paper was to investigate the substituent dependence of the 440 nm d-d transition band in arylferrocenes as well as the corresponding band in arylferricenium salts. A further aim of our work was to follow the charge-transfer complex formation of arylferrocenes with tetracyano-ethylene.

## Results and Discussion

In contrast to the good correlation of $\lambda_{max}$ of the d-d transition bands with $\sigma$ constants in the case of ferrocene analogues of chalcones[5], no simple correlation of this band was found for arylferrocenes. The data of Table 1 and Fig. 1 show that practically no substituent dependence of $\lambda_{max}$ is observed for derivatives with electron-donating substituents; a rather high substituent dependence of the 440 nm band was however observed in derivatives with strong electron with drawing substituents.

A similar behaviour also was found if $\lambda_{max}$ values of several arylferrocenes[11] were treated analogously. This phenomenon can be explained by the assumption that d-orbitals of the iron atom in ferrocene are widely separated in energy levels

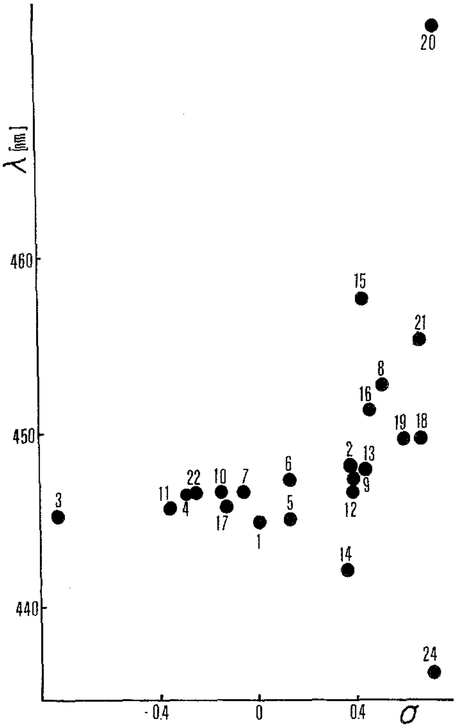

Fig. 1. Plot of $\lambda_{max}$ of the d-d transition band of arylferrocenes vs. $\sigma$-constants

(sensitive to the substituent effects) in derivatives with high covalent character of the *Fe-Cp* bond as is the case for ferrocene analogues of chalcones[5] but not for ferrocene and its alkyl derivatives.

Attempts to measure the charge-transfer band of arylferrocenes with *TCNE* failed. Due to the very low solubility of the starting materials in cyclohexane the charge-transfer bands located near 1 000 nm ($\varepsilon \sim 310$) have very low intensities and were observed only in the case of arylferrocenes with electron-donating substituents. As can be seen from Fig. 2 the charge-transfer band is rather complex and therefore no attempt has been made on a *Hammett* type correlation.

To increase the solubility of arylferrocenes and *TCNE* ethylacetate was used: Therein the rather complex CTB was observed as well as a new band near 700 nm which can be ascribed to the d-d transition of an arylferricenium cation[12]. The progress of arylferrocene oxidation was monitored in accord with Ref.[15] by the change of colour of the solution

Table 1. *Electronic spectra of arylferrocenes and of the corresponding arylferricenium salts*

| No. | *X* | Fc-$C_6H_4X$ | | Fc-$C_6H_4X^{+\text{fl}}$ | $\sigma(\sigma^+)$ | $E_{1/2}$[9][mV] |
|---|---|---|---|---|---|---|
| | | *n*-hexane $\lambda_{[nm]}$ | methanol $\lambda_{[nm]}$ | acetonitrile $\lambda_{[nm]}$ | | |
| 1 | H | 444.8 | 447.9 | 745 | 0.00 | 473 |
| 2 | *m*-Cl | 448 | 448.5 | 705 | 0.37 | – |
| 3 | *p*-$N(CH_3)_2$ | 445 | 447.6 | 1 300 | −0.83 (−1.70) | – |
| 4 | *p*-$OCH_3$ | 446.5 | 447.9 | 845 | −0.268 (−0.78) | – |
| 5 | *m*-$OCH_3$ | 445 | 448 | 750 | 0.115 (0.05) | 473 |
| 6 | *m*-OH | 447.1 | 447.3 | 740 | 0.12 | – |
| 7 | *m*-$C_2H_5$ | 446.6 | 447.8 | 750 | −0.07 | 464 |
| 8 | *p*-$COCH_3$ | 452.5 | 466.7 | 710 | 0.50 | 525 |
| 9 | *m*-Br | 447.5 | 540.4 | 710 | 0.39 | – |
| 10 | *p*-$C_2H_5$ | 446.4 | 448.7 | 760 | −0.151 | 447 |
| 11 | *p*-OH | 445.6 | 447.1 | 855 | −0.37 (−0.92) | – |
| 12 | *m*-$COCH_3$ | 446.5 | 437.1 | 720 | 0.376 | 506 |
| 13 | *m*-$CF_3$ | 447.8 | 450.5 | 715 | 0.43 | 525 |
| 14 | *m*-CHO | 442.1 | 433.7 | 700 | 0.35 | 516 |
| 15 | *p*-CHO | 457.4 | 474.2 | 700 | 0.42 | 536 |
| 16 | *p*-COO*Et* | 452.1 | 459.1 | 700 | 0.45 | 521 |
| 17 | 3,5-$CH_3$, $CH_3$ | 445.8 | 448.8 | 760 | −0.14 | 454 |
| 18 | 3-$CF_3$, 4-Cl | 449.5 | 452.3 | 710 | 0.66 | – |
| 19 | 3,4-Cl, Cl | 449.6 | 450.7 | 715 | 0.60 (0.51) | 528 |
| 20 | *p*-$NO_2$ | 473.7 | | – | 0.78 | 565 |
| 21 | *p*-CN | 455.7 | 461.2 | 690 | 0.66 | – |
| 22 | 3,4-$CH_3$, $CH_3$ | 446.5 | 448.0 | 790 | −0.24 | 439 |

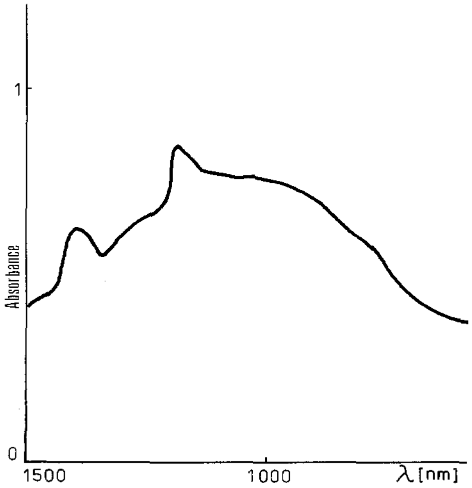

Fig. 2. UV-VIS spectrum of the charge-transfer complex formed between *Fc*-$C_6H_4OCH_{3(p)}$ and *TCNE* in cyclohexane

from orange to deep green. Oxidation was promoted by heating the solution for several hours at 70 °C. Derivatives with electron withdrawing substituents needed prolonged heating. The arylferricinium salts $ArFc^{(+)}\ PCNP^{(-)}$ were also prepared by heating equimolar quantities of the components in sealed tubes. Derivatives with electron withdrawing substituents had to be heated at temperatures up to 120 °C. Nevertheless our attempt to oxidise *p*-nitrophenyl ferrocene failed. The VIS and NIR spectra of the salts was proved by the absorption bands near 400 nm and 420 nm which are characteristic for a *PCNP* anion[13] (see Fig. 3) and also by the fact that there is no absorption band in the VIS spectra of arylferrocene or tetracyanoethylene near 700 nm (see Fig. 4). Since the d-d transition band near 700 nm was well developed in all derivatives under study and its position could be recorded with high precision we decided to study its substituent dependence. According to Fig. 5 an excellent *Hammett* correlation with $\sigma^+$ constants was observed (*p*-dimethylaminophenyl ferrocene was excluded).

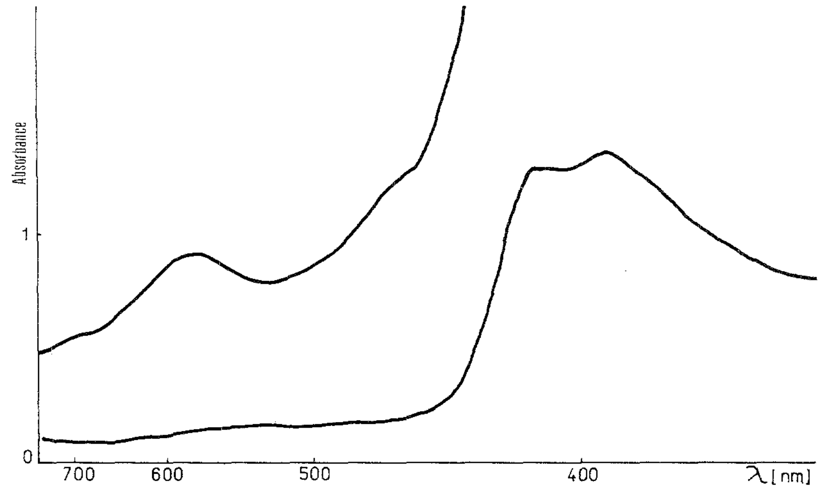

Fig. 3. UV-VIS spectrum of $Ph-Fc^{(+)}\ PCNP^{(-)}$ acetonitrile; $c = 0.8 \cdot 10^{-6}$ mol/dm$^3$ (300–500 nm) or 5.10$^5$ mol/dm$^3$ (500–700 nm, upper line)

$$\rho = -101.09; \qquad r = 0.974; \qquad s_\rho = \pm 5.66$$

To prove that the 700 nm band corresponds to the Fe d-d transition of arylferricinium salts we attempted to correlate the $E_{1/2}$ oxidation potantial with $\lambda_{\max}$ (Fig. 6). The $E_{1/2}$-value was taken from the literature[9] and good correlation was found for all $E_{1/2}$-values with the exception of the *p*-$OCH_3$

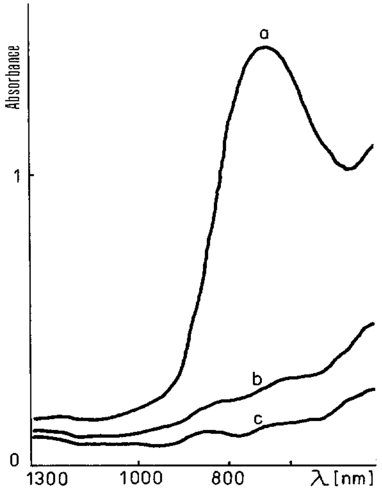

Fig. 4. VIS spectrum of *Ph*−*Fc*$^{(+)}$*PCNP*$^{(-)}$(*a*), *Ph*−*Fc* (*b*), and *TCNE* (*c*) (saturated solutions in acetonitrile)

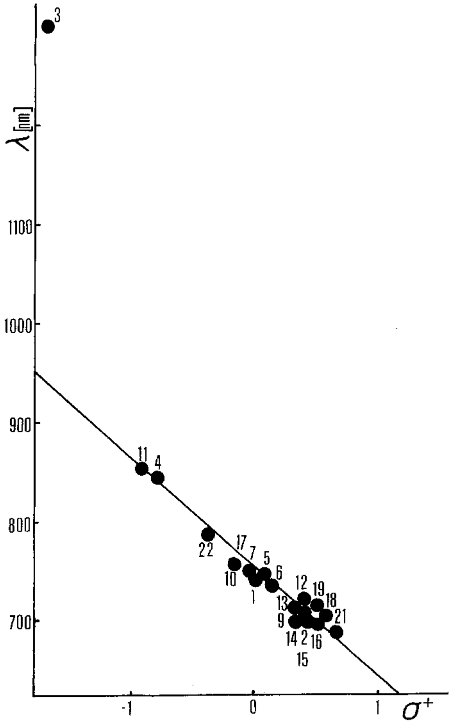

Fig. 5. *Hammett* correlation of $\lambda_{max}$ (d-d transition) of arylferricenium cation radicals with $\sigma^+$ constants

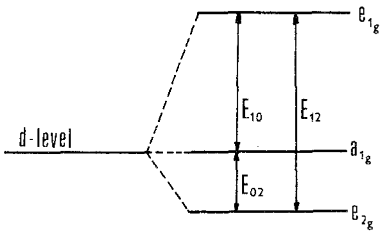

Fig. 6. Atomic orbitals of Fe in ferrocene derivatives

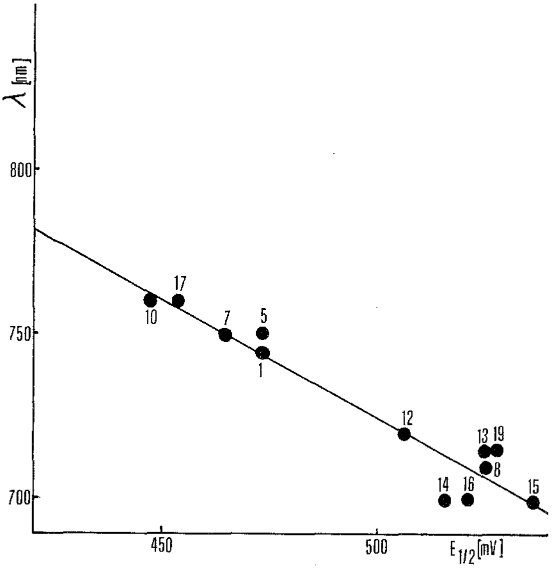

Fig. 7. Correlation of $\lambda_{max}$ (d-d transition) of arylferricenium cation radicals with $E_{1/2}$ oxidation potentials of the same compounds (taken from Ref.[9])

derivative which was not taken into the correlation. The slope is: $\rho = -0.710$; $r = 0.959$; $s_p = \pm 0.06$ (Fig. 7).

The observed different behaviour of arylferrocenes and arylferricenium salts may be rationalized by the relatively low covalency of the *Cp*-Fe bond which manifests itself in the high value of the parameter for phenylferrocene calculated by *Pavlik*[23] ($\beta = 0.38$) and the high covalency of this bond which can be foreseen for phenylferricenium on the basis of the localised charges on *Cp* and Fe which were calculated for Fe-protonated ferrocene by *Koridze*[24] ($-0.03$, $+0.06$).

## Experimental

Arylferrocenes were prepared and purified according to Ref.[6]. Tetracyanoethylene (Lachema, Brno) was sublimed (70 °C, 1.5 Pa) prior to use. The solvents used in this work were purified as described[22]. Visible and NIR spectra were recorded on a Perkin-Elmer 450 spectrophotometer. Visible spectra of arylferrocenes measured as $5.10^{-4}$ mol/dm$^3$ solutions in *n*-hexane and methanol are presented in Table 1. Visible and NMR spectra of charge-transfer complexes of *Fc*−*Ar* with *TCNE* in saturated solutions in cyclohexane were recorded as described in Ref.[10]. The arylferricenium salts $Ar-Fc^{(+)}\,PCNP^{(-)}$ were prepared either by heating equimolar amounts of arylferrocenes and tetracyanoethylene in ethyl acetate for 60–80 min at 70 °C or by heating equimolar quantities of the starting materials in sealed and evacuated (0.1 Pa) tubes at 80–120 °C for 12 h. Their spectra were measured in acetonitrile without further purification and are summarized in Table 1.

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