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ELECTRON DENSITY DISTRIBUTION IN FERROCENE ANALOGUES OF STILBENE. INTERACTION OF SUBSTITUENTS AND MOLECULAR GROUPS IN FERROCENE DERIVATIVES

ÁGNES G. NAGY *

Chemistry Department, Central Research Institute for Physics, 1121 Budapest (Hungary)

and STEFAN TOMA

Organic Chemistry Department, Comenius University, 84215 Bratislava (Czechoslovakia)

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Summary

Two techniques, ^{13}C NMR and cyclic voltammetry, are utilized to determine the change of electron density distribution caused by substituents in ferrocene analogues of stilbene. The interactions of substituents and some molecular groups in four series of ferrocene derivatives is discussed and the transmission coefficients of these groups are presented.

Introduction

The effect of substituents in ferrocene derivatives has recently been investigated. The variation of electron density (δ) distribution in the molecules was given numerically as a function of the electron-donating or electron-withdrawing strengths of the substituents in phenylferrocenes and ferrocene analogues of chalcone (Series I–III, Fig. 1) [1]. Here the electron density in ferrocene analogues of stilbene is shown by ^{13}C NMR and cyclic voltammetry and the interactions between the different groups and substituents of a molecule are discussed for four ferrocene series.

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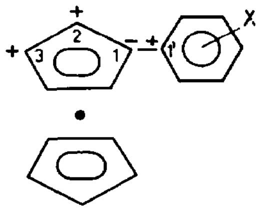
* To whom correspondence should be addressed.

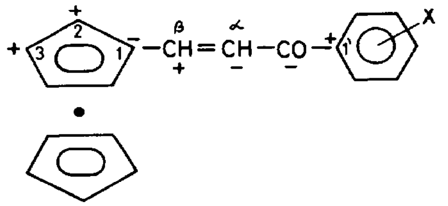
Results and discussion

(A) The chemical shift and oxidation potential values of the ferrocene analogues of stilbene (1-ferrocenyl-2-arylethylene, Fig. 1) are listed in Table 1. The values of $\Delta E_{1/2}$, the difference between the oxidation potentials of the substituted derivatives and the basic compound (X = H), are given in the fourth column of the table. The oxidation potential refers to the iron component of the ferrocenyl moiety. The $\Delta E_{1/2}$ values of the compounds are plotted against the ^{13}C NMR data in Fig. 2 and 3. The slope values and the intercepts of the curves are given in Table 2. For comparison of the results, some known data of Series I–III are presented in Table 3 [1].

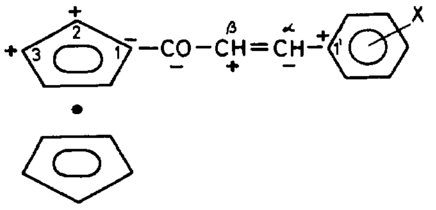
As shown in Fig. 2 and 3, a linear correlation can be seen between the $\Delta E_{1/2}$ values and the chemical shifts of the different carbon atoms of the molecules. The



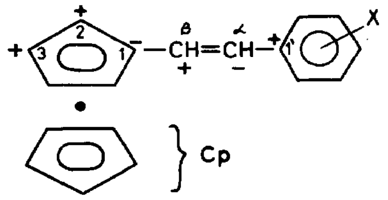
Phenylferrocene (series I)



1-Aryl-3-ferrocenyl-2-propene-1-one (X = H) (Series II)



3-Aryl-1-ferrocenyl-2-propene-1-one (X = H) (Series III)



1-Aryl-2-ferrocenylethylene (X = H) (Series IV)

Fig. 1. Ferrocene derivatives (Series I–IV). The signs of the slopes of the $\Delta E_{1/2}$ (ppm) curves are also shown. (The filled circles represent the iron atoms.)

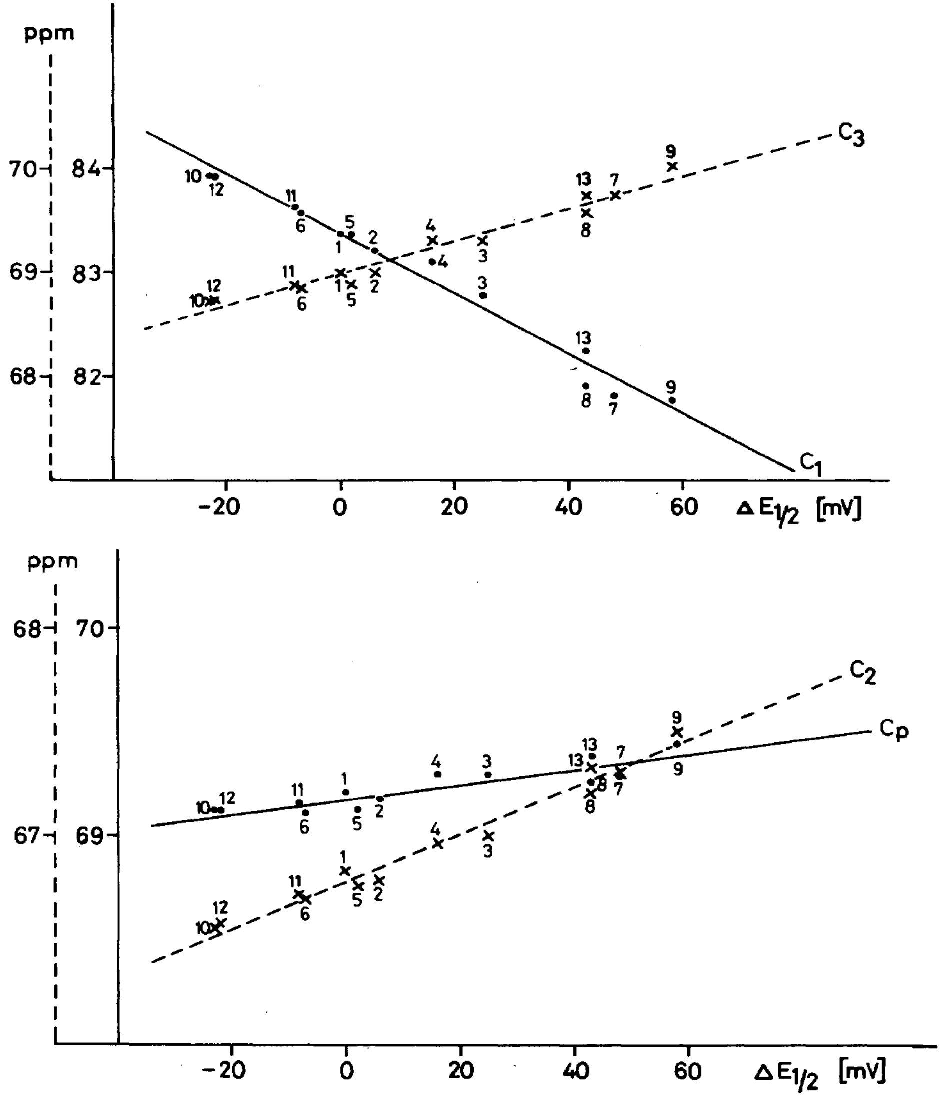


Fig. 2. Chemical shifts of C(1), C(3) and C(2), Cp in Series IV as a function of $\Delta E_{1/2}$.

signs of the C(1) and C_α curves are negative whereas those of curves Cp *, C_β and C(2), C(3) are positive (see Table 2). These signs indicate the trend of the variation in the δ distribution as a function of the electron-withdrawing or electron-donating strengths of the X substituents. The electron-withdrawing substituent, for example, increases the δ on the C(1) atom (downfield) simultaneously with a decrease of the δ on the C(2) and C(3) atoms of the Cp-ring. As mentioned in our earlier work, such a combination of these techniques enables the variation of δ on different carbon atoms of a molecule to be measured [1]. Accordingly, comparison of the measured slope values of the appropriate C atoms in Series I–III shows that C(3) has a higher slope

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* Cp = cyclopentadienyl ring.

TABLE 1

OXIDATION POTENTIALS AND ^{13}C CHEMICAL SHIFTS OF SERIES IV

Line number	Substituent (X)	$E_{1/2}$ (mV)	$\Delta E_{1/2}$ (mV)	C(1)	C(2)	C(3)	Cp ppm	C(1′)	C(2′)	C(3′)	C(4′)	C_β	C_α	σ
1	H	435 ± 2	–	83.37	69.01	66.84	69.21	137.83	125.74	128.57	126.72	126.84	126.01	0
2	*p*-F	441 ± 2	6	83.22	69.01	66.79	69.18	134.06	127.12	115.13	161.77	126.63	124.82	0.06
3	*m*-F	460 ± 2	25	82.78	69.30	67.04	69.30	140.27	111.99	163.26	113.44	128.52	124.77	0.34
4	*p*-Cl	451 ± 1	16	83.10	69.30	66.97	69.30	136.37	126.91	128.74	126.79	127.72	124.72	0.227
5	*m*-CH_3	437 ± 3	2	83.37	68.89	66.77	69.13	137.71	126.55	137.98	128.45	126.38	126.06	−0.07
6	*p*-CH_3	428 ± 1	−7	83.56	68.84	66.70	69.11	135.05	125.62	127.28	136.44	125.72	125.94	−0.17
7	*p*-CN	483 ± 2	48	81.83	69.74	67.31	69.30	142.31	125.94	132.37	109.37	131.59	123.84	0.66
8	*m*-NO_2	478 ± 2	43	81.91	69.56	67.22	69.27	139.59	119.93	148.72	120.99	131.40	123.31	0.710
9	*p*-NO_2	493 ± 3	58	81.78	70.04	67.50	69.45	144.41	125.89	124.23	145.97	132.91	123.45	0.778
10	*p*-OC_2H_5	412 ± 2	−23	83.95	68.72	66.55	69.13	130.57	126.86	114.63	158.03	124.40	125.69	−0.24
11	*p*-C_2H_5	427 ± 1	−8	83.63	68.87	66.72	69.16	135.34	125.74	128.11	135.44	125.79	125.99	−0.151
12	*p*-OCH_3	413 ± 2	−22	83.93	68.74	66.58	69.13	130.69	125.62	114.05	158.64	124.50	125.62	−0.268
13	*p*-CHO	478 ± 1	43	82.26	69.74	67.34	69.39	144.04	126.08	130.35	134.62	131.52	124.56	0.420

value than that of the C(2) atom, thereby confirming the assumption that the 2(5) and 3(4) carbon atoms of the Cp-ring correspond to the *ortho* and *para* positions of benzene, respectively [2–4]. Curves C_α and C_β have different signs which means that

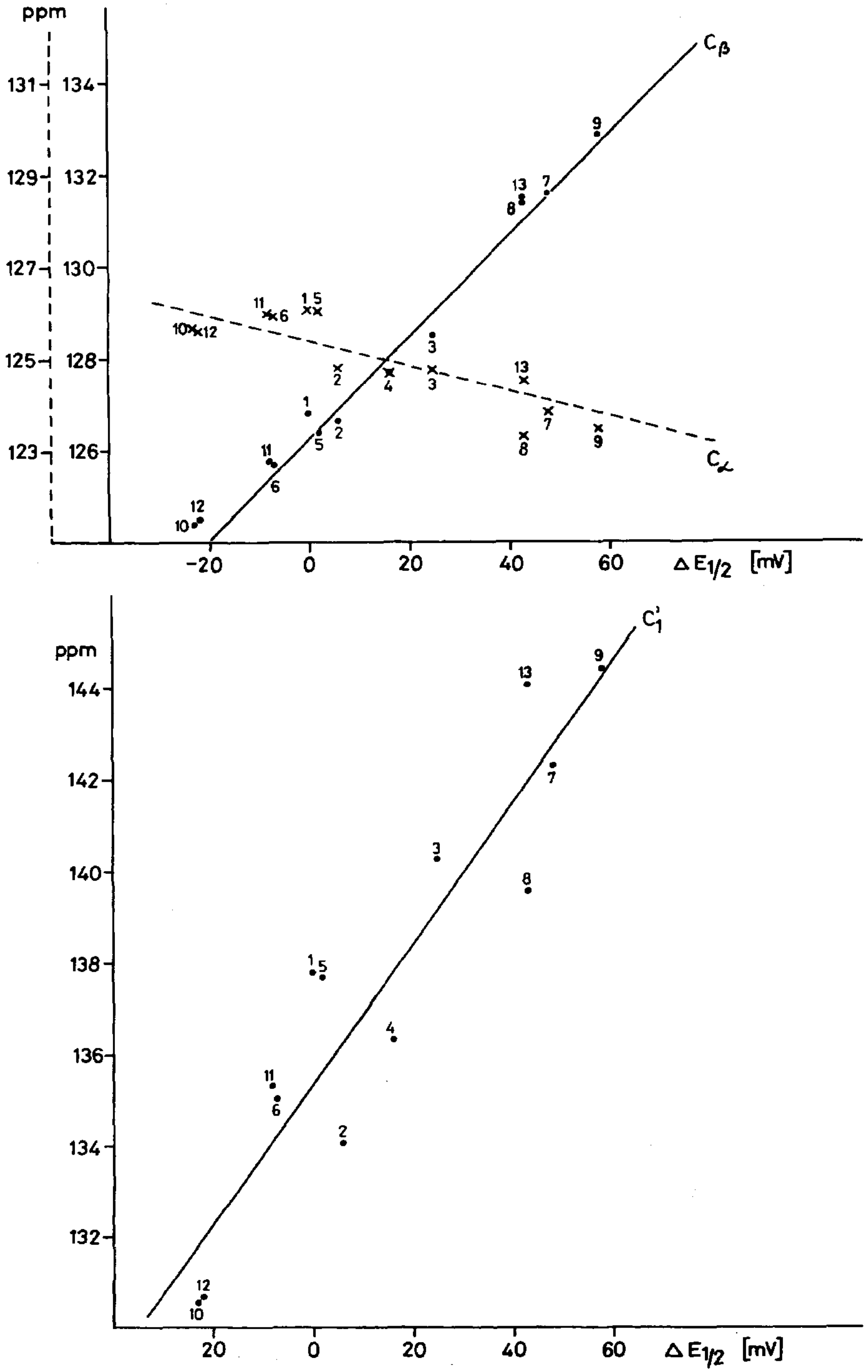

Fig. 3. Chemical shifts of C_α, C_β and C(1′) in Series IV as a function of $\Delta E_{1/2}$.

TABLE 2

SLOPE VALUES AND INTERCEPTS OF SERIES IV

Line number	Carbon number	Slope [a] (ppm/mV)	Intercept (ppm)	Correlation coefficient
1	C(1)	−2.85	83.36	0.99
2	C(2)	1.13	66.75	0.99
3	C(3)	1.57	68.99	0.98
4	Cp	0.36	69.19	0.90
5	C_α	−3.23	125.43	0.89
6	C_β	10.64	126.51	0.99

[a] All values to be multiplied by 10^{-2}.

TABLE 3

SLOPE VALUES AND INTERCEPTS OF SERIES I–IV

Series	Slope [a] C(1′) (ppm/mV)	Intercept (ppm)	Correlation coefficient	Slope [a] (carbonyl) (ppm/mV)	Intercept (ppm)	Correlation coefficient
Series I	11.19	138.27	0.92	–	–	–
Series II	15.83	137.51	0.66	−4.2	188.64	0.58
Series III	30.70	134.37	0.86	−2.1	192.62	0.84
Series IV	15.37	135.42	0.93	–	–	–

[a] All values to be multiplied by 10^{-2}.

the polarization of the vinylene is changed by the X substituents. With regard to the slope values of curves C_α and C_β, it should be taken into account that the oxidation potential measured at the iron component of the molecule is compared with the locally measured chemical shifts of the C_α and C_β atoms. As can be concluded from the effect of the carbonyl on the double bond (see Section B), the chemical shift value of C_α is decreased by an electron-withdrawing substituent. The intercept (IC) of curve C_α in the 1-aryl-2-ferrocenyl-ethylene is lower * than the IC of curve C_β (Table 2). Consequently the ferrocenyl is a slightly electron-donating group compared with the phenyl group. This is in good agreement with the fact that the phenyl group increases the oxidation potential of the ferrocene by 33 mV in the phenylferrocene [5].

Concerning the carbon atoms of phenyl in this series, only the curve of the C(1′) atom can be presented because of the scattered data of the C(2′), C(3′) and C(4′) atoms. The correlation coefficient of the curve C(1′) is low (Table 3) but in spite of this it is obvious that the slope of the curve is positive, that is, the electron density on C(1′) is decreased by an electron-withdrawing substituent.

Similarly to series I–III, the $\Delta E_{1/2}$ values of these ferrocene analogues of stilbene were also plotted vs. the Hammett constants (σ) in an attempt to find a correlation (Fig. 4). As expected, a linear correlation exists between the oxidation potentials and

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* In drawing our conclusions we considered the intercepts of the fitted curves because of the scattering of the measured values.

the σ values. The regression line, established by a least-squares fit, is:

$$\Delta E_{1/2} = 7.15 \times 10^{-2}\,\sigma + 1.3 \times 10^{-3}\ \text{V}$$

and the correlation coefficient is 0.98 (for 13 points). The equation of the directly substituted ferrocenes is known and the slope value (ρ) of the regression line is 0.45 (see Table 4 in ref. 6 and ref. 1). From the slope values (ρ_4/ρ) the transmission coefficient of the $C_6H_4CH{=}CH$ group is 0.16.

(B) From the structural point of view the ferrocene analogues of stilbene fit well with our earlier work, that is, with Series I–III [1]. To obtain more information about these derivatives it seems to be worthwhile to compare the results of these series.

In the basic compound (X = H) of Series II ($\text{Fc-}\underset{\beta}{\text{C}}\text{H=}\underset{\alpha}{\text{C}}\text{HCOC}_6\text{H}_5$) the strong electron-withdrawing carbonyl causes an upfield shift of the C_α atom (IC = 119

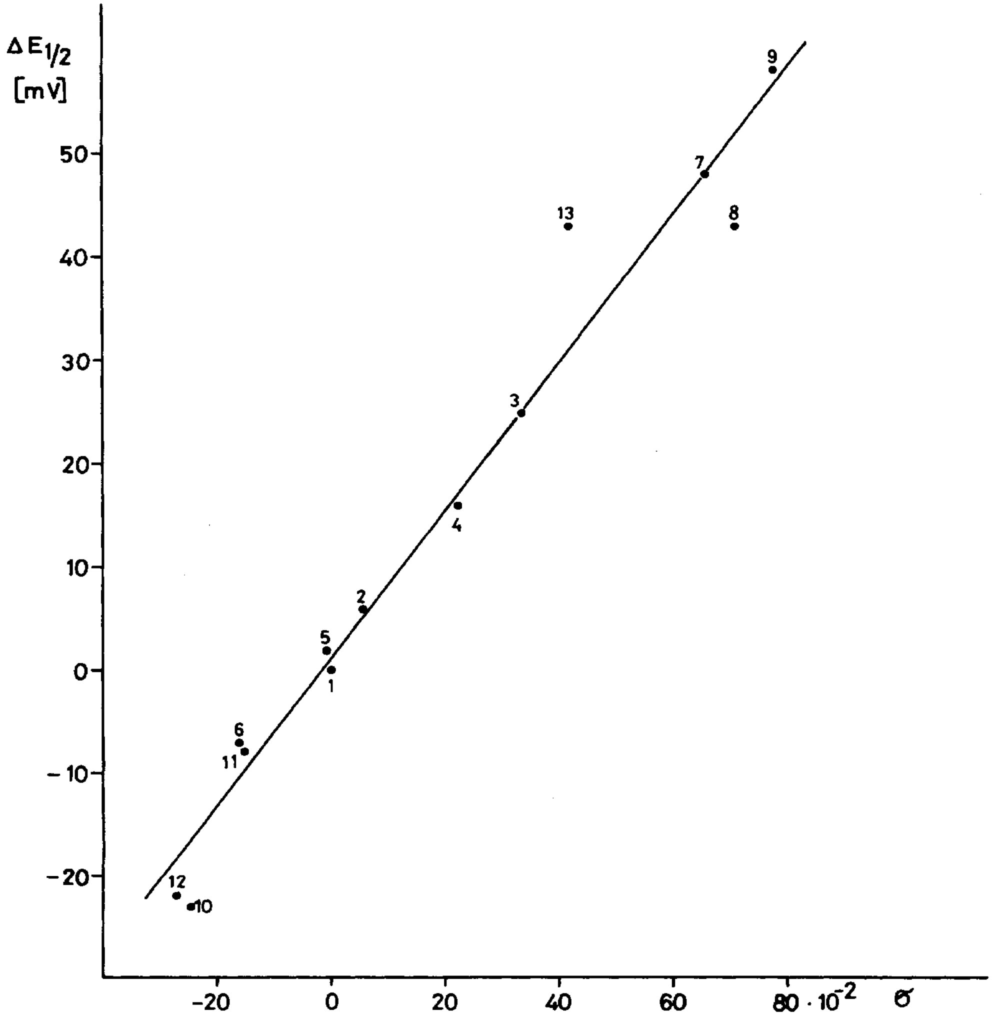

Fig. 4. Relationship between $\Delta E_{1/2}$ and the Hammett σ constants for Series IV.

TABLE 4

EQUATIONS OF THE $\Delta E_{1/2}(\sigma)$ CURVES

Series	Equations	Transmission coefficients
Directly substituted ferrocenes	$\Delta E_{1/2} = 45\times 10^{-2}\,\sigma + 2.2\times 10^{-2}$ V	–
Phenylferrocenes		
Series I	$\Delta E_{1/2} = 12.1\times 10^{-2}\,\sigma - 7.42\times 10^{-3}$ V	0.27
Series II	$\Delta E_{1/2} = 3\times 10^{-2}\,\sigma + 0.009\times 10^{-3}$ V	0.066
Series III	$\Delta E_{1/2} = 2.5\times 10^{-2}\,\sigma - 4.4\times 10^{-3}$ V	0.055
Series IV	$\Delta E_{1/2} = 7.15\times 10^{-2}\,\sigma + 1.3\times 10^{-3}$ V	0.16

ppm) simultaneously with a downfield shift of the C_β atom. Since the ferrocenyl is the electron-donating part of this molecule related to the phenyl (see Section A), the trend of the ferrocenyl- and the carbonyl-effects on C_β is similar [7]. C_β, which is the second atom to the carbonyl, has a chemical shift of 146.5 ppm. In the basic compound (X = H) of Series III ($\text{Fc-CO}\underset{\beta}{\text{C}}\text{H=}\underset{\alpha}{\text{C}}\text{HC}_6\text{H}_5$) the carbonyl decreases the chemical shift of C_β to 123 ppm and increases that of C_α. However, in this series the phenyl is bonded to C_α and the phenyl group is an electron-withdrawing substituent related to the ferrocenyl, so the phenyl works against the effect of the carbonyl on C_α. Consequently the chemical shift (IC) of C_α is 140.9 ppm.

It can be seen that the double bond of the vinylene group is strongly polarized in these series. Figure 5 shows the starting point, i.e. the positive and negative electron density shifts at the carbon atoms in the basic compounds. The X substituents of the phenyl group exert their electron-withdrawing or electron-donating effects on these molecules with perturbed electron densities. For all four series the signs of the $\Delta E_{1/2}$ (ppm) curves are also shown in Fig. 1. Two adjacent carbon atoms with negative signs can be found in series II and III. These show similar trends of the variation in δ distribution on these carbons; i.e. the δ values increase with increasing electron-withdrawing strengths of the X substituents and vice versa.

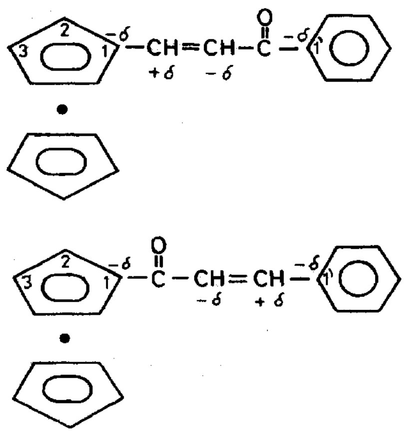

Fig. 5. Electron density shifts in the basic compounds of Series II and III.

As shown in Table 3, the signs of the C(1′) curves are positive in all four series, and the signs of the carbonyl curves are negative in Series II and III. The interactions of the X substituents and the other groups of the molecules are well demonstrated by the slope values of the C(1′) curves in Series II and III. The carbonyl of Series II works against the effect of X substituents causing a relatively small slope value (15.83) for C(1′), while the carbonyl of Series III, because of the vinylidene, results in a moderate decrease in the effect of the X substituents. Consequently the slope value is 30.7. As far as the negative signs of the carbonyl curves are concerned, this means an increase of the electron density on the carbon atom of the carbonyl group with increasing electron-withdrawing strengths of the substituents. On the other hand, the small slope value ($\sim 2.1 \times 10^{-2}$) of the carbonyl curve in Series III is in good agreement with the transmission coefficient of the vinylene group. It should be noticed, however, that the data of the carbonyls and C(1′) atoms are scattered (see the correlation coefficients in Table 3) so the conclusions need additional support.

Experimental

The 1-aryl-2-ferrocenylethylenes were prepared by the method of ref. 8. The purities of all compounds were checked by their melting points, TLC and by ^{1}H NMR. The physical constants of these compounds have also been given in ref. 8. The ^{13}C NMR spectra were obtained (Jeol FX-100 FT spectrometer with proton noise decoupling) at 25.05 MHz. All shifts were measured for deuterochloroform solution at 10% at ambient temperature. Tetramethylsilane (TMS) was used as the internal standard. The chemical shifts were determined with an accuracy of ±1 Hz (see ref. 9). The slope values of the $\Delta E_{1/2}$ (ppm) curves were calculated by the least-squares method. The oxidation potentials, $E_{1/2}$, of these ferrocene derivatives were measured by cyclic voltammetry in acetonitrile containing 0.1 *M* tetrabutylammonium perchlorate. The experimental conditions for the cyclic voltammetry were the same as those previously described [1].

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