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Substituent effects of phosphonate groups electronic repartition of π-conjugated ferrocene analogues of stilbene

Richard Frantz *, Jean-Olivier Durand, Gerard F. Lanneau

Laboratoire de Chimie Moléculaire et Organisation du Solide, UMR 5637, case 007, Université Montpellier 2, Place Eugène Bataillon, 34095 Montpellier cedex 05, France

Abstract

The synthesis of *para*-substituted ferrocene analogues of stilbene was performed by using the Heck reaction, starting from vinylferrocene. The variation of the electronic density of these compounds with the electronic withdrawing strength of the substituents was studied using ^{13}C NMR spectroscopy, absorption spectra and cyclic voltammetry. The correlation of Hammett constants with the redox properties of the substituted compounds using Nagy's method allowed us to revisit the determination of the Hammett constants of diethyl phosphonate ester and phosphonic acid substituents. Our measurements were in agreement with the literature except for the diethyl phosphonate group.
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1. Introduction

Phosphorus compounds are actually widely studied with potential applications in various domains, such as materials science, membranes, catalysts, sensors, light emitting diodes. Such interest relies in part upon the ability of functionalized phosphonates to strongly bind to metal oxides as solid supports [1–3].
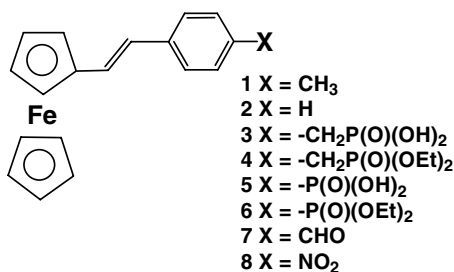
Ferrocene-terminated chromophores and ferrocene analogues of stilbene represent a new class of molecular materials, either due to their optoelectronic properties and/or in the field of supramolecular structures as redox-variable receptors. They form charge transfer complexes, generate mixed valent states by oxidation, and show non-linear optical properties [4–7]. Second-order NLO properties require the presence of polarizable electrons. This requirement is often attained by incorporating π-conjugated systems, like oligo phenylene vinylene (OPV) chromophores between electron donors and electron acceptors [8].

We recently published the synthesis of new ferrocenyl-terminated styryl phosphonates, **3–6** (Scheme 1) and their use for the functionalization of metal oxide nanoparticles [9]. Their applications in optoelectronics would suppose an enhanced effect of hyperpolarisability associated with a large difference between the donor/acceptor terminating substituents. It has been known for many years that there is a good correlation between the oxidation potentials of a series of structurally similar substituted aromatic compounds and the Hammett constants of the substituents [10]. The purpose of the present paper is to estimate the incidence of phosphono substituents upon the variation of the electronic density of substituted ferrocenyl stilbene **3–6**. Thus, we revisited the synthesis of four ferrocene analogues of stilbene **1, 2, 7** and **8** with electron withdrawing and electron-donating substituent by using the Heck reaction. The correlation of the substituent effects with the redox properties of the compounds following the method developed by Nagy and co-worker [13a] allowed us to revisit the Hammett constants of the phosphono groups.

* Corresponding author. Tel.: +334-67-14-30-38; fax: +334-67-14-38-52.

E-mail address: richard.frantz@chiorg.unige.ch (R. Frantz).

1 X = CH₃
2 X = H
3 X = -CH₂P(O)(OH)₂
4 X = -CH₂P(O)(OEt)₂
5 X = -P(O)(OH)₂
6 X = -P(O)(OEt)₂
7 X = CHO
8 X = NO₂

Scheme 1. Ferrocenyl-terminated styryl phosphonates.

2. Results and discussion

The oxidation of ferrocene derivatives depends on the electronic character of the substituents. Already in 1961, Mc Ewen and co-workers [11] noted a linear correlation between the Hammett substituent constants and the redox potentials of phenyl-ferrocenes from chronopotentiometric measurements. Tirouflet et al. [12] reported polarographic and oscillopolarographic data, emphasising the interest of ferrocenyl compounds to determine Hammett coefficients of typical substituents, difficult to attain with benzene analogs.

Later, Nagy presented a general Hammett correlation study of substituted ferrocenes, using cyclic voltammetry and ^{13}C NMR spectroscopy. The variation of electron density distribution [13] was estimated experimentally as a function of the electronic strength of the substituents in phenyl-ferrocenes and ferrocene analogues of stilbenes, including compounds **1**, **2**, **7** and **8** which were synthesized by the Wittig reaction. The authors observed a very good correlation of the oxidation potentials ($E_{1/2}$) of the molecules with the Hammett constants of the substituents as well as with the ^{13}C chemical shifts for carbon atoms with different positions in the ferrocenyl moiety.

The oxidation potential ($E_{1/2}$) of these compounds was measured by cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium perchlorate. ^{13}C NMR spectra were recorded in deuterochloroform solution at 10% at ambient temperature. Such experimental conditions could not be used with phosphonic derivatives **3**–**6**, which are better solubilized in DMSO.

We therefore envisioned the strictly controlled synthesis of the reference compounds **1**, **2**, **7** and **8** in order to obtain appropriate calibration data for the comparison of the electronic effects.

The Wittig reaction was extensively used for the synthesis of this kind of compounds [14]. Transition metal catalysis such as olefin metathesis [15a] and Heck's reaction under Jeffery's conditions [15b,15c] have been only scarcely described. The ferrocenyl E-*trans* stilbene reference compounds **1**, **2**, **7** and **8** were obtained by the Heck coupling reaction between vinyl-

ferrocene (commercial) and the *para*-substituted bromoarenes, in homogeneous conditions [9a] (Scheme 2).

The method of choice for the characterization of redox processes of oligomeric aromatic systems is cyclic voltammetry. It provides information on both thermodynamic and kinetic data of electron transfer reactions and allows a precise analysis of multi-step redox mechanisms [18].

Oxidation potential values of substituted ferrocene analogues of stilbene are listed in Table 1. The value of $\Delta E_{1/2} = E_{1/2}(\text{FcX}) - E_{1/2}(\text{FcH})$ is the difference between the oxidation potential of the substituted derivative and the basic compound **2** (X = H).

All compounds studied show a reversible single-electron oxidation wave due to the oxidation of Fe(II)–Fe(III) in the ferrocene fragment. The oxidation peak potentials (E_{pa}) are in the same range expected for ferrocene analogues of stilbene (versus SCE) [13]. Data presented in Table 1 show that the oxidation potential is sensitive to the substituents on the phenyl group of the compounds **1**–**8**. $\Delta(E_{1/2})$ increases as the electron withdrawing group ability increases from compound **1** to **8**. The donor effect of the methyl group is shown by the negative value of $\Delta(E_{1/2})$. The $\Delta(E_{1/2})$ value of compounds **5** and **6** confirms the important electron withdrawing effect of the phosphonate/phosphonic groups, not far from the aldehyde group of compound **7**. The presence of the CH₂ group in **3** and **4** strongly reduces the electron withdrawing effect of the phosphonate as shown by the lower $\Delta(E_{1/2})$ value. As noted for carboxylate/carboxylic acids substituted ferrocenes [19], the change is minimal if the E_{pa} values of the phosphonates are compared to those of their corresponding phosphonic acids.

The electronic absorption spectra were recorded in DMSO, at a concentration of 10^{-3} M (Fig. 1). Electronic absorption spectra of compounds **1**–**8** present two weak bands in the visible region, between 320 and 350 nm and between 455 and 518 nm. The highest energy band is attributed to the π–π* transition [16]. The lower
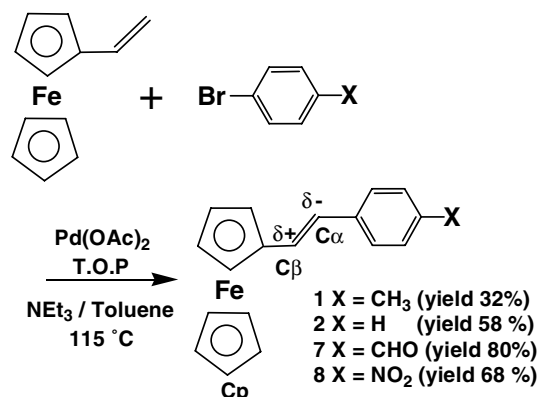

1 X = CH₃ (yield 32%)
2 X = H (yield 58 %)
7 X = CHO (yield 80%)
8 X = NO₂ (yield 68 %)

Scheme 2. Synthesis of compounds **1**, **2**, **7** and **8**.

Table 1
Cyclic voltammetric data, Hammett substituent constants $\sigma_p{}^a$, selected ^{13}C NMR data, and λ_{dd} (nm) absorption bands of the compounds **1–8**

Number	Substituent X	$E_{1/2}$ (mV)	$\Delta(E_{1/2})$ (mV)	$\sigma_p{}^a$	$\sigma_p{}^b$	$C\alpha$ (ppm)	$C\beta$ (ppm)	Cp (ppm)	UVλ_{dd}(nm)
1	CH$_3$	457	−12	−0.17		126.7	126.4	69.60	455
2	H	469	0	0		126.5	127.9	69.85	458
3	–CH$_2$P(O)(OH)$_2$	470	1	0	0	127.0	126.2	69.85	456
4	–CH$_2$P(O)(OEt)$_2$	475	6	0.06	0.06	126.2	127.5	69.84	457
5	–P(O)(OH)$_2$	501	32	0.42	0.40	125.8	130.0	69.92	463
6	–P(O)(OEt)$_2$	505	36	0.60	0.45	125.2	131.3	69.96	467
7	–C(O)H	509	40	0.42		125.2	132.6	70.03	485
8	–NO$_2$	525	56	0.78		124.2	134.3	70.09	518

[a] Values taken from [10].
[b] Revised value obtained from Fig. 3.
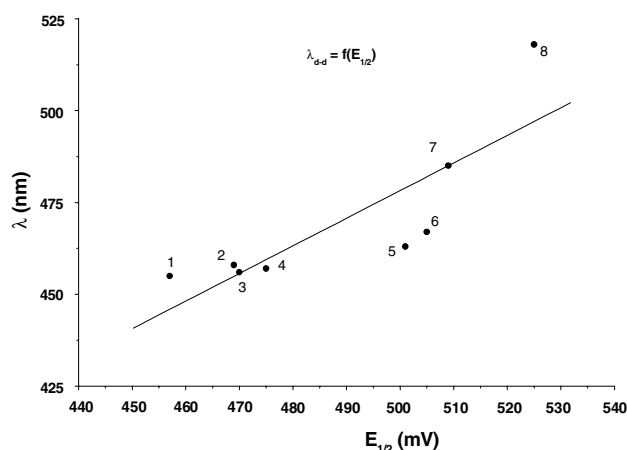
Fig. 1. Correlation of λ_{dd} with $E_{1/2}$. linear fit: $\lambda_{dd} = 0.7515E_{1/2} + 102.47$ correlation coefficient: 0.83.

energy band (Table 1), is assigned to the d–d transition of iron [16]. Both bands are red-shifted with increasing withdrawing properties of the substituents [17] as shown by the correlation between wavelength and oxidation potential reported in Fig. 1. However the correlation coefficient is low for a linear fit, which suggests that other parameters (solvatation) than pure electronic effects of the substituents are involved [20–22].

The variation of the electron density distribution with the electron withdrawing strength of the substituents can be characterized by the variation of the ^{13}C chemical shift. The correlation between the oxidation potential and the ^{13}C NMR data for carbons Cα, Cβ, and Cp, reported in Table 1, are presented in Fig. 2. In these cases, a linear correlation can be seen with good correlation coefficients. The slope of the curve is negative for Cα, positive for Cβ and Cp. The electronic density increases for Cα and decreases for Cβ and Cp by increasing the electron withdrawing strength of the substituents of compounds **1–8**, confirming the polarization of the double bond. These results are in agreement with those observed by Tirouflet et al. [12]. In order to quantify these electronic effects, we revisited the

determination of the Hammett constants, σ_p of the phosphono substituents of molecules **3–6** by a correlation and linear fit between the oxidation potential of compounds **1–8** and the Hammett σ_p constants of compounds **1**, **2**, **7** and **8**.

The curve is shown in Fig. 3. An excellent correlation coefficient was found. We obtained: $\sigma_p = 0$ for CH$_2$PO$_3$H$_2$, $\sigma_p = 0.06$ for CH$_2$PO$_3$Et$_2$ in agreement with the literature (Table 1). These groups have no electron withdrawing effect due to the presence of the CH$_2$ linker. We obtained: $\sigma_p = 0.40$ for PO$_3$H$_2$, $\sigma_p = 0.45$ for PO$_3$Et$_2$, the Hammett constants of these groups are in the range of that of the CHO substituent. Literature gives $\sigma_p = 0.42$ for PO$_3$H$_2$, but 0.60 for PO$_3$Et$_2$ (Table 1), which is higher than our determination. However, literature also gives $\sigma_p = 0.45$ for CO$_2$H, CO$_2$Me and CO$_2$Et [9]. There are no differences of electron withdrawing strength between carboxylic acid and carboxylate ethyl or methyl esters substituents. Therefore a similar behaviour of PO$_3$Et$_2$ and PO$_3$H$_2$ is not unexpected, as shown by our cyclic voltammetry measurements and Hammett constant determination.

In conclusion, the Heck reaction has proved to be a general method for the stereoselective synthesis of ferrocene analogues of stilbene. The variation of the electron density of these compounds with the substituents were described by correlations of ^{13}C NMR shifts with cyclic voltammetry following Nagy's method. These linear correlations allowed us to revisit the determination of the Hammett constants of the phosphono substituents: CH$_2$PO$_3$H$_2$, CH$_2$PO$_3$Et$_2$, PO$_3$H$_2$, PO$_3$Et$_2$. We found similar electron withdrawing behaviour for phosphonic acid and diethyl phosphonate substituents, and the value σ_p of the diethyl phosphonate was revised to 0.45.

3. Experimental

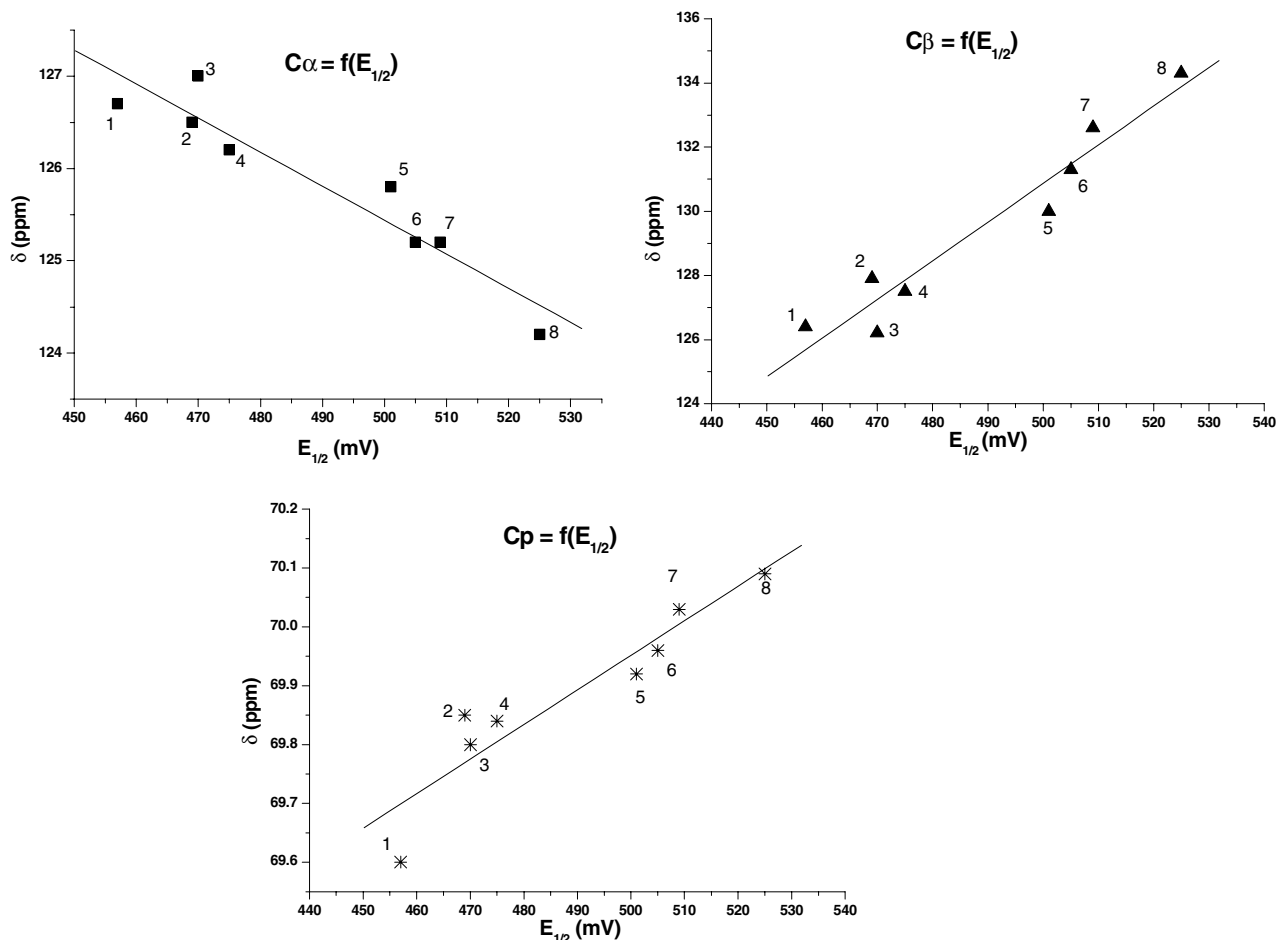Vinylferrocene was purchased from Lancaster; palladium acetate was purchased from Avocado, and these

Fig. 2. Correlation of Cα, Cβ, Cp with $E_{1/2}$. Linear fit: Cα $= -0.0369E_{1/2} + 143.88$ correlation coefficient 0.95. Cβ $= 0.1206E_{1/2} + 70.58$ Correlation coefficient 0.97. Cp $= 0.0059E_{1/2} + 67.01$ correlation coefficient 0.93.
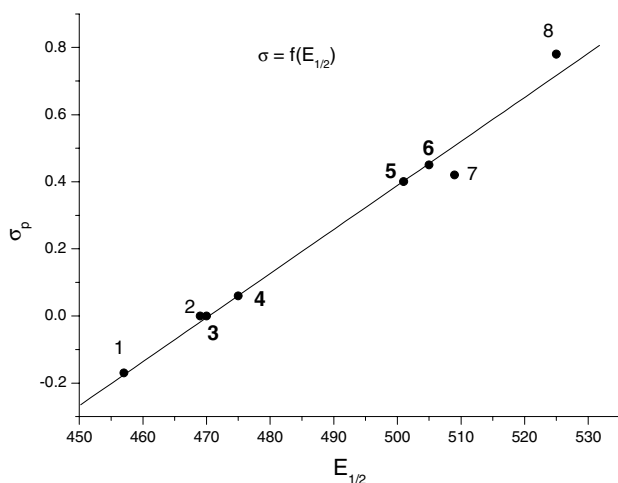

Fig. 3. Correlation between σ_p and $E_{1/2}$. Linear fit: $\sigma_p = 0.0131 E_{1/2} - 6.17$ correlation coefficient: 0.99.

products were used without further purification. All reactions and manipulations were carried out under an atmosphere of argon. Solvents were dried by standard

methods and were distilled prior to use. ^{1}H NMR spectra, ^{13}C NMR spectra were obtained on Bruker AC-200 spectrometer. UV spectra were registered on a Perkin–Elmer λ 14 instrument. The regression lines were established by the least-squares fit method. The oxidation potentials $E_{1/2}$ were registered by cyclic voltammetry in DMSO containing $n\text{Bu}_4\text{NPF}_6\text{C} = 0.1$ M, with a radiometer analytical voltalab PGZ 100 apparatus.

General procedure for the Heck reaction: see [9]

The products were purified by column chromatography on silica gel (eluents: pentane **1**, **2** and toluene **7**, **8**). Yields: **1**: 32%, **2**: 58%, **7**: 80%, **8**: 68%.

Analytical data for compounds **1**, **2**, **7** and **8** are described in [13b]

Compound 1. RMN[1]H (DMSO d[6] δ ppm): 2.34 (s, 3H, CH₃); 4.19 (s, 5H, Cp); 4.36 (t, 2H, $^3J_{HH} = 1.8$ Hz, H Cp); 4.60 (t, 2H, $^3J_{HH} = 1.70$ Hz, H Cp); 6.78 (d, 1H, $^3J_{HH} = 16.3$ Hz, H vinyl); 6.96 (d, 1H, $^3J_{HH} = 16.2$ Hz, H vinyl); 7.20 (d, 2H, $^3J_{HH} = 7.9$ Hz, H arom); 7.44 (d, 2H, $^3J_{HH} = 8.0$ Hz, H arom).

RMN[13]C DEPT (DMSO d[6], δ ppm) : 21.7 (s, CH₃); 67.5 (s, CH, Cp); 69.0 (s, CH, Cp); 69.6 (s, Cp); 125.5

(CH arom); 126.4 (Cβ vinyl); 126.7 (Cα vinyl); 133.6 (CH arom).

Compound **2**. RMN^{1}H (DMSO d^6, δ ppm): 4.19 (s, 5H, Cp); 4.37 (t, 2H, $^3J_{HH}$ = 1.6 Hz, H Cp); 4.61 (t, 2H, $^3J_{HH}$ = 1.6 Hz, H Cp); 6.82 (d, 1H, $^3J_{HH}$ = 16.2 Hz, H vinyl); 7.03 (d, 1H, $^3J_{HH}$ = 16.2 Hz, H vinyl); 7.27 (t, 1H, $^3J_{HH}$ = 7.1 Hz, H arom); 7.39 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H arom); 7.54 (d, 2H, $^3J_{HH}$ = 7.5 Hz, H arom).

RMN^{13}C DEPT (DMSO d^6, δ ppm) : 67.6 (s, CH, Cp); 69.8 (s, CH, Cp); 69.9 (s, Cp); 126.5 (Cα vinyl); 126.5 (CH arom); 127.5 (CH arom); 127.9 (Cβ vinyl); 129.5 (CH arom).

Compound **7**. RMN^{1}H (DMSO d^6, δ ppm): 4.18 (s, 5H, Cp); 4.41 (t, 2H, $^3J_{HH}$ = 1,6 Hz Cp); 4.65 (t, 3H, $^3J_{HH}$ = 1,6 Hz, H Cp); 6.92 (d, 1H, $^3J_{HH}$ = 16,2 Hz, vinyl); 7.30 (d, 1H, $^3J_{HH}$ = 16.2 Hz, H vinyl); 7.72 (d, 2H, $^3J_{HH}$ = 8.3 Hz, H arom); 7.88 (d, 2H, $^3J_{HH}$ = 8.3 Hz, H arom), 9.97 (s, 1H CHO).

RMN^{13}C DEPT (DMSO d^6, δppm): 68.2 (s, CH, Cp); 70.0 (s, Cp); 70.5 (s, CH, Cp); 125.2 (Cα vinyl); 127.0 (CH arom); 131.0 (CH arom); 132.6 (Cβ vinyl), 193.2 (CHO).

Compound **8**. RMN^{1}H (DMSO d^6, δ ppm): 4.23 (s, 5H, Cp); 4.47 (s, 3H, H Cp); 4.70 (s, 3H, H Cp); 6.97 (d, 1H, $^3J_{HH}$ = 16.1 Hz, H vinyl); 7.37 (d, 1H, $^3J_{HH}$ = 16.1 Hz, H vinyl); 7.79 (d, 2H, $^3J_{HH}$ = 8.2 Hz, H arom); 8.23 (d, 2H, $^3J_{HH}$ = 8.2 Hz, H arom).

RMN^{13}C DEPT (DMSO d^6, δ ppm): 68.4 (s, CH, Cp); 70.1 (s, Cp); 70.7 (s, CH, Cp); 124.2 (Cα vinyl); 124.9 (CH arom); 127.2 (CH arom); 134.3 (Cβ vinyl).

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