Journal of Organometallic Chemistry, 390 (1990) 217–225
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20722

Spectroscopic investigation of chalcone-analogous ferrocenes *ortho*-substituted in the aromatic ring

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(Received January 20th, 1990)

Abstract

Chalcone-analogous ferrocenes *ortho*-substituted in the aromatic ring were prepared and their oxidation potentials measured by cyclic voltammetry. *Ortho*-substituted analogues show a greater increase in oxidation potentials than the *meta*- and *para*-analogues. The configurations, conformations and electron distributions of these compounds were investigated by IR, ^{1}H and ^{13}C NMR techniques. Linear correlations were found between the electronegativity of the substituents and the oxidation potentials, and between the IR carbonyl frequencies, some carbon chemical shifts and the oxidation potentials.

Introduction

In contrast to *meta*- and *para*-substituted analogues, no correlation has been found between the electronegativity of the substituents and the chemical and spectroscopic features of *ortho*-substituted benzene derivatives [1–3]. In spite of intensive studies [4–6], *ortho*-substituent constants [σ^o) corresponding to the Hammett and Taft Constants deduced for *para*- and *metal*-substituted benzene compounds have not been revealed. There are large differences in the published σ^o values and their applications to different systems have not given acceptable results.

In the present study IR, H and ^{13}C NMR spectroscopic investigations as well as cyclic voltammetric studies of the chalcone-analogous ferrocene derivatives (**1–8**) are described which demonstrate the connection between chemical structures and spectroscopic properties. Though the "*ortho* effect" makes the interpretation of the spectroscopic results from compounds **1–8** more difficult, for that very reason it offers an attractive and interesting task.

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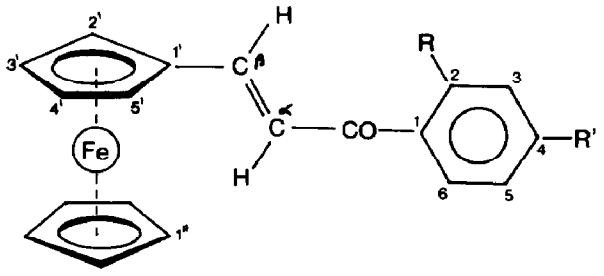


1 (R = R': H)
2 (R: OMe, R': H)
3 (R: Me, R': H)
4 (R: OH, R': H)
5 (R: Cl, R': H)
6 (R: NO_2, R': H)
7 (R = R': Cl)
8 (R: NH_2, R': H)

Results and discussion

1. Oxidation potentials

Correlations have recently been demonstrated [7,8] between the Hammett substituent constants ($\sigma^{p,m}$), the oxidation potentials ($E_{1/2}$) and most of the ^{13}C NMR chemical shifts in the *para*- and *meta*-substituted analogues of compounds **1**–**8** (Fig. 1, 2). In the case of *ortho*-substituted analogues good correlation has been found only between the δ(C-1′) and $E_{1/2}$ values (Fig. 2). However, the substituents cause a two- or three-fold change in the oxidation potentials and in the chemical shifts δ(C-1′). Pseudo σ^o constants can be determined from the $\sigma^{p,m}/E_{1/2}$ curve of the

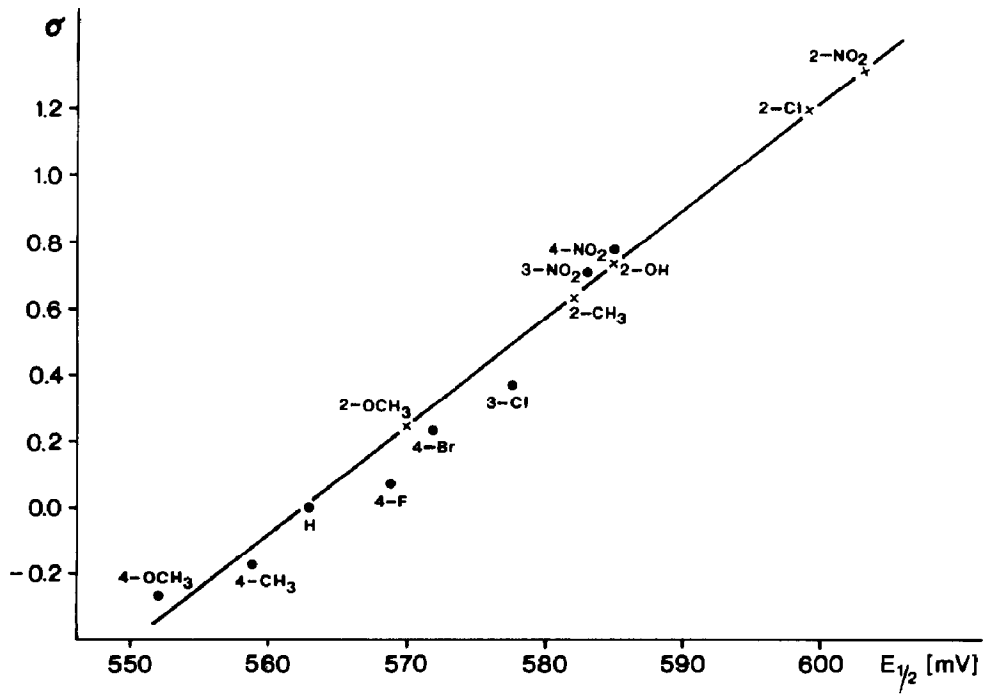


Fig. 1. Relationship between the oxidation potential of chalcone-analogous ferrocenes and Hammett substituent constant.

para- and *meta*-substituted analogues (Fig. 1). All of these pseudo σ^o "constants" are shifted in the positive direction relative to the $\sigma^{p,m}$ values.

2. *^{1}H NMR spectra*

The assumed constitution and the stereohomogeneity of compounds **1–8** are proved by their ^{1}H NMR spectra (Table 1). The ^3J(H-α,H-β) coupling constants of 15.0–16.0 Hz suggest that all the compounds investigated are *E*-isomers [9a,10]; *Z*-isomers could not be traced in our substances. The ^{1}H NMR chemical shift differences in the series **1–8** are very small. Only in compounds **1** and **4** were significantly higher chemical shifts for H-α, H-β and ArH-6 atoms measured. This fact proves the coplanarity of the benzene ring and the -enone moiety in **1** and **4**. This coplanarity is stabilized by the stronger conjugation in compound **1** unsubstituted in the *ortho* position and by the chelation in **4**. Evidence for chelate structure of **4** [9b] comes from the high downfield shift of the OH signal (13.0 ppm) and by the disappearance of the ν(OH) band from the IR spectrum [11a]. The conjugation of the carbonyl and olefinic bonds decreases the electron density at the H-α atom and makes it more pronounced at the H-β atom due to the predominance of the **b** limiting structure in the mesomeric system [9c]. On the other hand, the anisotropic effect of the carbonyl and olefinic groups decreases the shielding about the near and coplanar ArH-2,6 and ArH-6 atoms in **1** and **4**, respectively [9d].

The absence of similar effects from compounds **2**, **3**, **5–8** proves their non-planar conformation, a result of the steric hindrance of the *ortho* substituents. Since the spectral data of the C=O and C=C bonds of the latter compounds do not show any significant difference from the coplanar analogues **1** and **4**, the coplanarity of the

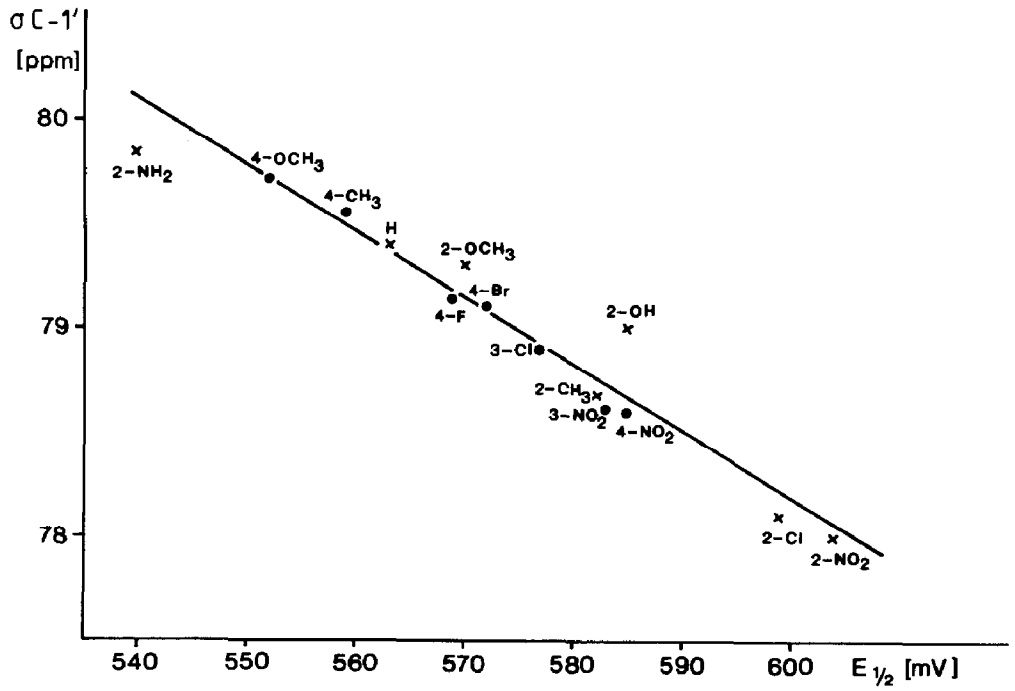


Fig. 2. Chemical shift of C-1′ atoms versus oxidation potential ($E_{1/2}$).

Table 1

Characteristic IR frequencies (cm^{-1}) and ^1H NMR chemical shifts ($CDCl_3$ solution, δ(TMS) 0 ppm) of compounds **1–8** at 250 MHz

Compound	C=O band		C=C band	ArH [a] s(5H)	ArH(subst. [b])		H-*A* *d*(1H) [c]	H-β *d*(1H) [c]	ArH(aryl), 4×1H				CH_3 s(3H)
	KBr	$CDCl_3$			≈ s(2H)	≈ s(2H)			H-3dd	H-4td	H-5td	H-6dd	
1	1662		1602	4.17	4.48	4.59	7.12	7.75	7.4–7.6 [d]	7.4–7.6 [d]	7.4–7.6 [d]	7.98 [e]	–
2	1660	1650 [f]	1590	4.16	4.44	4.53	6.90	7.47	6.98	7.44	7.03	7.54	3.88
3	1627	1655 [d]	1610	4.14	4.45	4.51	6.70	≈ 7.4 [g]	7.2–7.5 [g]	7.2–7.5 [g]	7.2–7.5 [g]	7.2–7.5 [g]	2.42
4	1633		1556	4.20	4.54	4.63	7.24	7.90	7.02	7.48	6.92	7.85	13.05 [h]
5	1641	1630 [f]	1608	4.18	4.49	4.53	6.70	7.32 [g]	7.3–7.5 [g]	7.3–7.5 [g]	7.5–7.5 [g]		–
6	1643	1635 [f]	1603	4.16	4.48 [i]	4.48 [i]	6.59	7.11	8.15	7.64	7.76	7.46	–
7	1650		1590	4.19	5.50	4.55	6.68	7.34 [g]	7.48	–	≈ 7.36 [g]	≈ 7.36 [g]	–
8	1634		1614	4.16	4.43	4.56	7.24	7.66	~ 6.7 [g]	7.25	~ 6.7 [g]	7.80	6.3 [j]

[a/b] CP: unsubstituted/substituted cyclopentadiene ring. [c] J(H-α,H-β): 15.5 ± 0.5 Hz. [d] Coalesced multiplets of 3H total intensity. [e] H-2,6 signal of 2H intensity. [f] Two further maxima at about 1610 and 1588 cm^{-1}. [g] Overlapping signals. [g] OH-signal, s (1H). [i] Singlet, in DMSO-d_6 2× ≈ s at 4.58 and 4.77 ppm. [j] NH_2-signal, s(2H).

Table 2

^{13}C NMR chemical shifts (δ(TMS) 0 ppm) of compounds **1–8** in $CDCl_3$ solution fo 20 MHz [a]

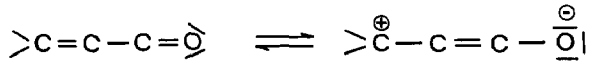
Compound	C=O	C-α	C-β	C-1′ [b]	C-2′,5′ [b]	C-3′,4′ [b]	C-1″ [c]	C-1 [d]	C-2 [d]	C-3 [d]	C-4 [d]	C-5 [d]	C-6 [d]
1	189.5	119.2	146.4	79.1	68.9	71.2	69.6	138.6	128.2 [e]	128.2 [e]	132.1	128.3 [e]	128.3 [e]
2	192.6	124.9	145.4	79.3	69.0	71.1	69.8	130.00	157.8	111.9	132.1	120.7	129.95
3	196.2	124.4	148.1	78.7	69.0	71.4	69.8	136.3	139.7	127.6	131.1	125.3	129.9
4	192.9	118.7 [f]	1478	79.0	69.3	71.8	70.0	120.2	163.7	117.0	135.8	118.7 [f]	129.4
5	192.5	123.6	148.5	78.1	68.9	71.4	69.5	130.6 [f]	139.4	128.7	130.6 [f]	126.5	129.8
6	191.7	124.1 [e]	148.5	77.8	68.9	71.9	69.9	136.4	146.9	123.1 [e]	130.1	133.7	128.6
7	192.0	123.5	149.5	78.2	69.3	71.9	69.9	132.0	136.3	130.1 [f]	138.1	127.3	130.1 [f]
8	191.2	117.3	144.4	79.8	68.8	71.0	69.7	119.5	150.9	115.8	133.8	120.3	130.7

[a] Measuring frequency is 63 MHz for compounds **3**, **7** and **8**. Further signals: CH_3: 55.7 (**2**), 20.0 (**3**). [b/c] Substituted/unsubstituted cyclopentadiene ring. [d] Benzene ring. [e] Reversed assignments may also be possible. [f] Two overlapping lines.

-enone group in series **1–8** is evident. Thus, the *ortho* substituents force the aromatic ring out of the -enone plane. This interpretation is supported by the upfield shift by 5.1 ppm of the C-α line in the ^{13}C NMR spectrum of **1** and **4** relative to the other compounds. In other words, the steric hindrance between the H-α and the *ortho* aryl hydrogens in **1** and **4** is manifested in stronger shielding. This field effect (steric compression shift [12]) is not found in compounds **2**, **3** and **5–8**. Regarding the non-planar structure of this series higher oxidation potentials than in the *meta*- and *para*-substituted analogues are quite plausible. The "higher electron affinity" of the substituents in the *ortho*-position can be explained by the absence of the $+M$-effect, since in the *meta*- and *para*-substituted compounds the $+M$-effect moderates the $-I$-effect.

3. ^{13}C NMR spectra

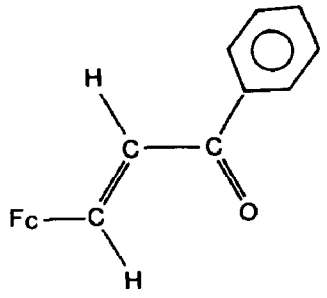
The chemical shifts of the carbonyl lines in the *ortho*-substituted series (Table 2) are higher by about 4 ppm than the analogous shifts of the *para*-substituted compounds [10]. These downfield shifts indicate a reduced density of electrons about the carbonyl carbon, a consequence of the lack of $+M$-effect in the *para*-substituted analogues. The unchanged chemical shifts of the C-β atoms show that these downfield shifts do not originate from the predominance of the **b** limiting structure in the **a** $\rightleftarrows$ **b** mesomeric system. The pfield shifts of the C-α lines, as mentioned above, are due to the field effect. The δ(C-A′) values are proportional to the oxidation potentials (Fig. 2) as is found in the *para*-substituted analogous [8]. The electron-attracting substituents increase the electron density at the C-1′ atoms, while the electron-donating substituents do not have the opposite effect, because of the suppressing of the $+M$-effect mentioned above (except for **8**).



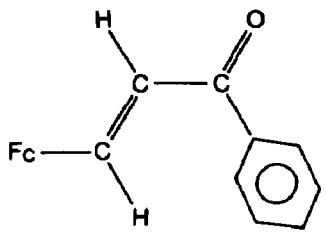
a b

4. IR measurements and the S-cis-S-trans isomerism

In the compounds **1–8** a conformational equilibrium may be formed by the rotations around both the C-1′–C_β and C_α–CO bonds in addition to that around the CO–C_{Ar} bond. The first of these is not influenced by the substitution of the benzene ring, and the chemical equivalence of the C-2′,5′ and H-2′,5′ atoms having identical chemical shifts can be regarded as evidence of free rotation. There are two favoured coplanar forms (*S-cis*, **c** and *S-trans*, **d**) among the rotamers formed by the rotation around the C-α–CO bond. IR spectra are often used to study **c** $\rightleftarrows$ **d** type conformational equilibria [4,11b,13], and an investigation of *meta*- and *para*-substituted analogues of the compounds **1–8** has also been reported [14]. For chalcones, the **c**/**d** ratio has been found to be 6/1 [13], while a conformative homogeneous *S-cis* structure was proposed for the ferrocene analogues from the IR data [14]. The *S-cis* form is preferred because of the strong steric hindrance between the H-β atom and the *ortho*-hydrogens of the benzene ring in the *S-trans* isomer. Due to their non-planar structure, this steric hindrance does not occur in compounds **2**, **3** and **5–8**, consequently the possibility of a change in the **c** $\rightleftarrows$ **d** equilibrium compared to the *meta*- and *para*-substituted analogues or to compounds **1** and **4** should be considered. There are no sharp carbonyl bands in the IR spectra of the chloroform solution but broad overlapped absorption maxima covering a wide range of 50–70



c



d

cm^{-1} can be found. Therefore, it is difficult to get reliable information about the conformations from the IR data on the basis of the empirical rules suggested in the literature [13]. In any case the submaxima suggest a conformational equilibrium. The probability of equilibrium is also supported by the H-α and H-β chemical shifts. Both signals are shifted upfield to approximately the same extent ($\sim$ 0.4 ppm), i.e. the $\Delta\delta$(H-α,H-β) shift differences are practically the same. If the conformational equilibrium had changed significantly in favour of the **d** form, these differences would have been less marked. The H-α atom, would tend to lose its shielding when subjected to the anisotropic effect of the coplanar carbonyl group, while the less effectively shielded H-β atom would be drawn closer to the non-planar benzene ring, whose anisotropy would increase the shielding about the H-β atom.

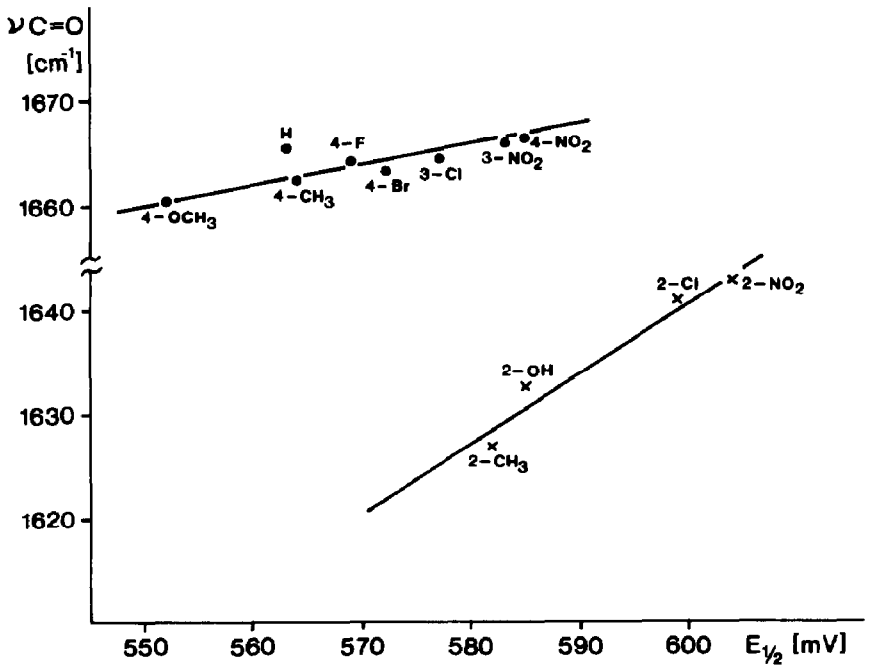


Fig. 3. Frequency of carbonyl (ν(C=O)) IR bands against oxidation potential in *para*-, *meta*- and *ortho*-substituted chalcone-analogous ferrocenes (2-NH_2, 2-OCH_3 omitted)

The ν(C=O) frequencies measured in KBr disks are significantly lower than those of the *para*- and *meta*-substituted analogues and this is in good agreement with the above assumption, i.e. that the $+M$-effect is suppressed in the non-planar structure. This effect increases the carbonyl bond-order and thereby the ν(C=O) frequencies of the *meta*- and *para*-substituted analogues. In view of this, the linear relationship inferred between the ν(C=O) (IR) and the $E_{1/2}$ data is quite plausible (Fig. 3).

Experimental

The compounds **1–8** were prepared by base-catalysed Claisen–Schmidt condensation with the corresponding substituted acetophenones and ferrocene-aldehyde [15,16]. The solvent was (abs.) ethanol in the presence of NaOH and the reaction was followed by cyclic voltammetry. Details on the preparation and physical constants of the compounds **1–8** are given in ref. 17. The oxidation potentials were measured by cyclic voltammetry in acetonitrile containing 0.1 *M* tetrabutylammonium perchlorate. A three electrode cell was used in which the working and auxiliary electrodes were Pt and the reference electrode was Ag/AgCl (sat.) The measurements were carried out in an oxygen-free nitrogen atmosphere using internal standards, viz. ferrocene (440 mV) and dibenzoylferrocene (901 mV). The measurements were made at a scan rate of 100 mV/s and the potential range was 1.2 V (EF 427 potentiostat with functional generator was used).

IR spectra were run in KBr pellets or $CDCl_3$ solution on a Bruker IFS-113v vacuum optic FT-spectrometer equipped with an Aspect 2000 computer.

^{1}H and ^{13}C NMR spectra were recorded on Bruker WM-250 and WP-80-SY spectrometers at 250.13 MHz (^{1}H) and 62.89 MHz or 20.15 MHz (^{13}C), respectively (cf. Table 2). Typical parameters for ^{1}H measurements are as follows: internal reference: TMS, lock signal: the ^{2}H resonance of the solvent, pulse width: 1 μs ($\sim 20°$ flip angle), acquisition time 2.05 s for 16 K data points. Lorentzian exponential muliplication was used for signal-to-noise enhancement (line with 0.7 Hz).

^{13}C spectra with the following parameters were measured at 62.89 and 20.15 MHz, $\sim 30°$ flip angle, pulse width 7.5 and 3.5 μs, BB decoupling with ~ 3.5 and ~ 1 W power, memory size 32 and 16 k for 16 and 5 kHz spectral width, exponential multiplications of line-width 2.0 and 1.0 Hz, repetition rate 2 s, number of scans 1 ± 0.3k, for **2** and **4** 21 k, acquisition time 0.5 and 1.5 s.

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