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

II *. Ferrocenyl–CO–CH=CH–aryl-type compounds

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Abstract

Chalcone-analogous ferrocenes of the type Fc–CO–CH=CH–Ar, *ortho*-substituted in the aromatic ring were prepared. Their conformations and electron distributions were investigated by cyclic voltammetry, IR, ^{1}H and ^{13}C NMR spectroscopy. The spectroscopic properties measured for this series were compared with those of *para*-substituted analogues and with data for structural isomers synthesized and studied earlier and having the aryl and ferrocenyl groups bonded to the enone moiety in reversed positions (Fc–CH=CH–CO–Ar). In contrast with the isomers investigated earlier, the new series are coplanar and the *S-cis* ⇄ *S-trans* conformational equilibria are shifted in favour of the former.

Introduction

Continuing our studies on intramolecular conjugative interactions, chalcone analogous ferrocene derivatives **1**–**7** (Type II) have been synthesized [1]. Their structural isomers, the analogous ferrocenyl–CH=CH–CO–aryl-type compounds (Type I) were described earlier [1,2].

For steric reasons, in the series I, the coplanar arrangement of the carbonyl and phenyl substituents is not possible, consequently the conjugative interactions and mesomeric effects of substituents are diminished. Exceptions may be those *ortho*-substituted derivatives (i.e., OH, NH_2) in which a strong chelate hydrogen bond may stabilize the coplanar structure. In the present paper the results of cyclic voltammetric, IR, ^{1}H-NMR, and ^{13}C-NMR studies of Type II compounds will be reported and discussed. Results obtained for compounds Type I and II will also be compared.

* For Part I see ref. 2.

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Table 1

Oxidation potentials. Characteristic IR frequencies (in KBr discs, cm^{-1}) and ^1H NMR chemical shifts (in $CDCl_3$ solution, δ(TMS) = 0 ppm) of compounds **1**–**7** at 250 MHz

Compound	$E_{1/2}$ (mV)	ν(C=O)	ν(C=C)	ArH [a] s (5H) [a]	ArH-2′,5′ ~ s (2H) [b]	ArH-3′,4′ ~ s (2H) [b]	H-α d (1H) [c]	H-β d (1H) [c]	ArH(aryl), 2–5H [d] H-3	H-4	H-5	H-6	CH_3 s (3H)
1	686	1649	1593	4.21	4.92	4.59	7.13	7.80		7.42 [e]		7.65 [f]	–
2	676	1645	1585	4.21	4.90	4.56	7.23	8.10	~ 7.0 [e]	7.40 [g]	~ 7.0 [e]	7.64 [h]	3.93
3	686	1646	1587	4.22	4.91	4.57	7.05	8.08		~ 7.25 [e]		7.68 [h]	2.50
4	681	1644	1585	4.21	4.90	4.56	7.25 [e]	8.05		~ 6.9 [i] –		~ 7.25 [e]	3.83 3.88
5	697	1648	1585	4.22	4.91	4.59	7.10	8.15	~ 7.3 [e]	7.43 [g]	7.3 [e]	7.73 [h]	–
6 [j]	700	1650	1592	4.24	4.91	4.62	6.95	8.14	~ 8.05 [h]	~ 7.6 [g]		~ 7.7 [e]	–
7 [j]	695	1649	1602 [k] 1572 [k]	4.24	4.93	4.61	6.83	8.24	7.68 [l]	–	–	7.02 [l]	4.00 4.05

[a] Unsubstituted cyclopentadiene ring. [b] Substituted cyclopentadiene ring. [c] J(H-α,H-β): 15.6 ± 0.2 Hz. [d] Total intensity of the ArH(aryl) signals is 5H for **1**, 4H for **2**, **3**, **5** and **6**, 3H for **4** and 2H for **7**. [e] Coalesced signals m(3H) for **1** and **3**, m(2H) for **2**, **4**, **5** and **6**. [f] H-2,6 signal of the phenyl substituent (2H). [g] ~ t (1H). [h] ~ d (1H). [i] Overlapping signals, m (2H). [j] Ir bands of the nitro group: 1518, 1343 and 849 (**6**); 1521 and 1333 (**7**). [k] Split band pair. [l] s (1H).

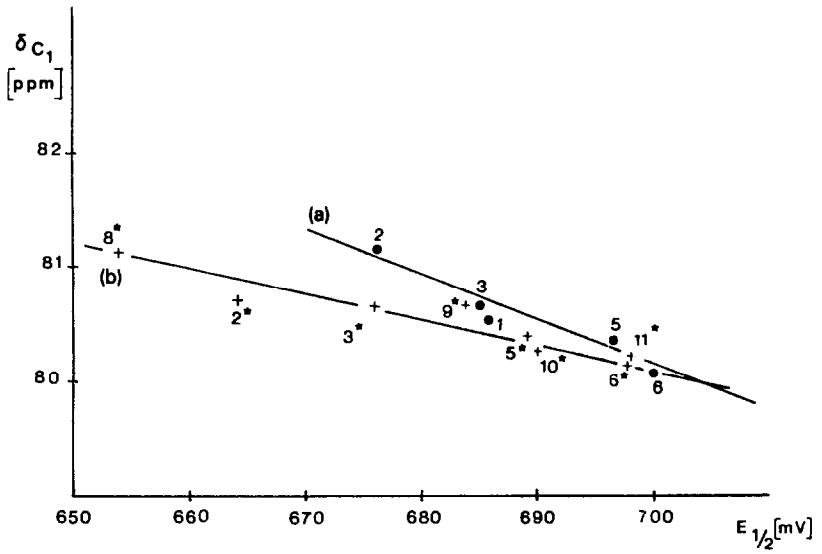
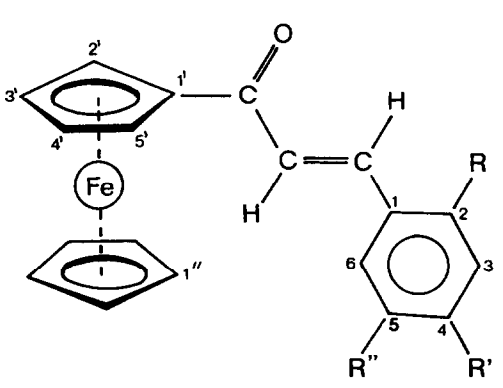


Fig. 1. ^{13}C-NMR chemical shifts of the C_1 atoms in Type II compounds: (a) **1–3**, **5** and **6** (●) and (b) their *para*-substituted analogues **2***, **3***, **5***, **6***, **8*** (R = NMe), **9*** (R = F), **10*** (R = Br) and **11*** (R = CN) (+), respectively, versus oxidation potential $E_{1/2}$.

Cyclic voltammetric results

The oxidation potentials $E_{1/2}$ of compounds **1–7** (Table 1) are somewhat greater than those of the corresponding *para*-substituted derivatives [3]. The difference, however, seems to be rather slight (Fig. 1). Reverse substituent effects [4] have not been observed, i.e. electron attracting substituents should have the same character both in *para*-, and *ortho*-positions. The strong reverse effect observed in the case of compounds Type I may be interpreted by mesomeric effects being weaker due to the non-planar structure, as mentioned above. Thus, the lack of the reverse effect suggests a coplanar stucture for compounds **1–7**.



1 (R = R'= R": H)

2 (R: OCH_3, R'= R": H)

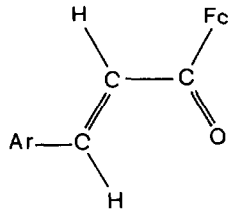
3 (R: CH_3, R'= R": H)

4 (R = R": OCH_3, R': H)

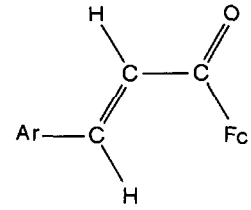
5 (R: Cl, R'= R": H)

6 (R: NO_2, R'= R": H)

7 (R: NO_2, R'= R": OCH_3)



A



B

Ar: aryl
Fc: ferrocenyl

IR spectra and *S-cis–S-trans* isomerism

In the case of Type II compounds conformational equilibria exist due to rotation not only around the C_β–C(Ar) bond but also around the C_α–C(=O) and C_1(Fc)–C(=O) bonds. Substitution of the benzene ring has no influence on the freedom of rotation around the latter two bonds and the chemical shift equivalence of C-2′,5′ as well as H-2′,5′ atoms suggests free rotation. Rotation around the C_α–C(=O) bond may lead to an equilibrium of *S-cis* (**A**) and *S-trans* (**B**) conformers.

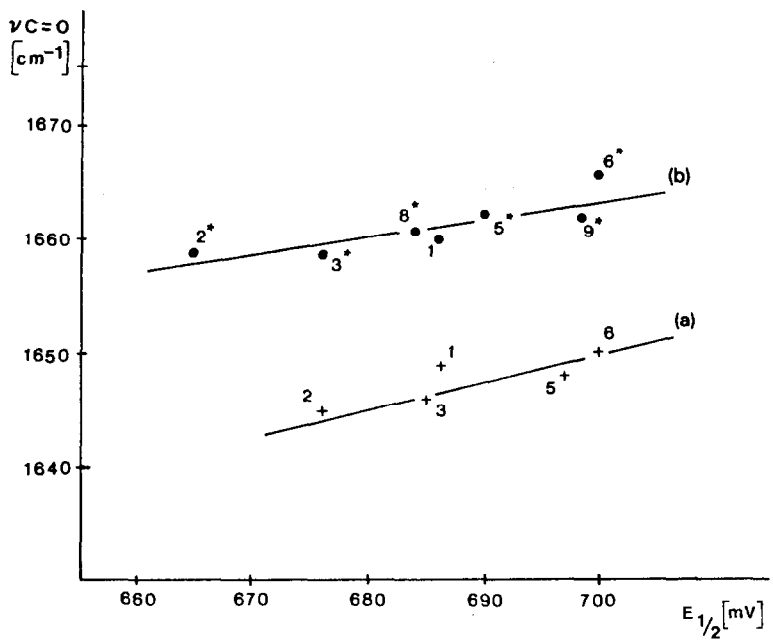


Fig. 2. The IR-frequencies of carbonyl stretching vibrations (νC=O) in Type II compounds: (a) **1–3**, **5** and **6** in KBr discs (+) and (b) their *para*-substituted analogues **2***, **3***, **5***, **6***, **8*** (R = F) and **9*** (R = CN) in CCl_4 solution (●), respectively, against oxidation potential $E_{1/2}$.

IR spectra may be useful for studying this conformational equilibrium [5,6]. In the case of compounds **1–7** the differences between ν(C=O) and ν(C=C) stretching frequencies in KBr are 50–70 cm^{-1} (Table 1). This may be an indication of the predominance of *S-cis* (**A**) conformer.

The ν(C=O) frequencies as measured in KBr are somewhat smaller than those of the *para*-substituted analogues measured in CCl_4 solution, but within the series of *ortho*-substituted compounds **1–7**, a relative good correlation was found between the ν(C=O) and $E_{1/2}$ values (Fig. 2). The gradients of the lines corresponding to the *ortho*- and *para*-substituted derivatives are practically identical. As the ν(C=O) frequency for compound **1** (X = H) measured in a KBr disc is very near to line **a**, the decrease of ν(C=O) values may be mainly due to different medium of the measurements.

^{1}H NMR spectra

The ^{1}H NMR data (Table 2) prove beyond doubt the expected constitution and stereohomogeneity of the compounds studied. The value of ^3J(H-α,H-β) coupling constants ($\sim$ 15.6 Hz) may be considered as firm proof that compounds **1–7** are homogeneous *E* isomers in all cases [7a]. No traces of *Z* isomers were detected. Only an insignificant variation of chemical shifts was observed within the series studied.

The chemical shift differences $\Delta\delta$(H-α,H-β) (their average being 1.05 ppm for compounds **2–7**) are significantly greater than those of Type I compounds ($\Delta\delta \sim 0.55$ ppm) and of *para*-substituted derivatives ($\sim$ 0.65 ppm). This difference from that of series I may be explained by changes in the polarisation of the mesomeric enone system $-C{=}C-C{=}O \leftrightarrow C^+-C{=}C-O^-$. In series II involving non-branching conjugation the polarized limiting case predominates (due to continuous conjugation, while in series I having branching conjugation the polarization is suppressed) [7a].

The differences between *ortho-para* pairs in series II, in accordance with measured oxidation potentials, precludes a non-planar structure for the *ortho*-isomers (observed for some compounds of Type I), because this would cause an effect of opposite sign. The increase of $\Delta\delta$ values cannot be interpreted as an anisotropic effect of *ortho*-substituents of the benzene ring, as this was also observed for the *ortho*-methyl compound **3**. From this substituent no deshielding effect can be expected. A possible explanation may be that in the conformation equilibrium **A** $\rightleftarrows$ **B** the *S-cis* form (**A**) predominates in the *ortho*-substituted II-Type series. In this conformation the carbonyl group lies near to the H-β atom and its anisotropy deshields it [7b] (the H-β signal exhibits a paramagnetic shift). As any change in **A** $\rightleftarrows$ **B** conformational equilibrium hardly influences the electron distribution of the enone system, the shielding around the H-α atom does not change, therefore the shift difference $\Delta\delta$(H-α,H-β) necessarily increases. This is in accordance with our NMR data (Table 1), as well as with conclusions drawn from IR data, and implies that the **B** form predominates in the **A** $\rightleftarrows$ **B** conformational equilibrium of *para*-substituted compounds. This means that in conformer **B** a considerable steric hindrance should exist between the *ortho*-substituted benzene ring and the ferrocenyl group, and this is avoided by *ortho*-substituted II-Type compounds, when rotating into the **A** conformation.

Table 2

^{13}C NMR chemical shifts (δ(TMS) = 0 ppm) of compounds **1–7** in $CDCl_3$ solution at 20 or 63 MHz [a]

Compound	ν(C=O)	ν(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-6 [d]	C-3 [d]	C-5 [d]	C-4 [d]
1	192.8	123.4	140.9	80.9	69.8	72.2	70.1	135.5	129.0		128.3		130.1
2	193.4	124.4	136.4	81.2	69.8	72.4	70.1	124.6	158.9	129.0	111.6	120.9	131.2
3	192.7	124.4 [e]	138.4	80.7	69.7	72.6	70.0	134.2	138.0	130.8 [f]	129.7 [f]	126.3 [e,g]	126.3 [e,g]
4	193.3	124.4	136.1	80.9	69.8	72.5	70.1	125.0	153.3 [e]	116.3	141.1	153.0 [e]	112.6
5	192.5	126.1	136.5	80.4	69.8	72.8	70.1	133.6 [e]	135.2 [e]	130.6 [f]	130.2 [f]	127.0 [h]	127.8 [h]
6	192.4	124.9	135.9	80.1	70.0	73.0	70.3	131.7	149.0	129.9 [e]	128.7 [e]	133.2	129.3 [e]
7	192.7	127.5	137.0	79.9	70.0	72.9	70.2	126.4	141.5	110.5	108.2	153.2	149.8

[a] 'Measuring frequency was 20.14 MHz for **1**, **2** and **6**, and 62.89 MHz for **3–5** and **7**, respectively; Further signals, CH_3, s (3H): 55.7 (**2**), 19.9 (**3**), 55.9 and 56.2 (**4**), 56.5 and 56.6 (**7**). [b] Substituted cyclopentadiene ring. [c] Unsubstituted cyclopentadiene ring. [d] Aryl group. [e,f,h] Reversed assignments may also be possible. [g] Two overlapping lines.

^{13}C NMR spectra

The ^{13}C NMR chemical shifts (Table 2) of carbonyl carbons does not show any changes, compared to *para*-substituted derivatives. This indicates an unchanged conjugation (coplanar structure).

The lines of C-β atoms of *ortho*-substituted derivatives show an upfield shift, compared with those of *para*-substituted analogues. This can be considered as steric compression shifts [8] due to steric hindrance between the *ortho*-substituents and the H-β atom in conformer **A**. This field effect is a further proof of the supposed coplanar structure, and the predominance of *S-cis* form.

The shielding of the C-α atom changes apparently capriciously in response to the simultaneous actions of different effects. Among these the following may play a role: (a) the change in anisotropy of ferrocenyl moiety (influenced by shift in the **A** $\rightleftarrows$ **B** equilibrium); (b) strong hydrogen bonding between H-β atom and the *ortho*-nitro substituent [6], or the corresponding weaker intramolecular interaction with the methoxy-oxygen and chlorine atoms, respectively, in the case of compounds **2** and **5**, due to their influence on the electron distribution.

The C_1 chemical shift in contrast with that of Type I compounds does not seem to be sensitive to the substitution of benzene ring. This is fully explained by the weaker conjugation in the branching enone-system of Type II series.

Experimental

The syntheses of compounds **1**–**7** have been published elsewhere [1]. The elemental analysis data are in good agreement ($\pm 0.2\%$) with the theoretical values. Melting points (uncorrected) are as follows (°C): Ref. [9] (**1**), 141 (**2**), 114 (**3**), 115 (**4**), 105 (**5**), 140 (**6**) and 168 (**7**).

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 atomosphere using internal standards, viz. ferrocene (440 mV) and dibenzoyl-ferrocene (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 discs on a Bruker IFS-113v vacuum optic FT-spectrometer equipped with an Aspect 2000 computer. ^1H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ solution in 5 or 10 mm tubes, at room temperature, on a Bruker WM 250 (^1H, ^{13}C) or WP 80-SY (^{13}C) FT-spectrometer controlled by an Aspect 2000 computer at 250.13 (^1H) and 62.89 or 20.14 (^{13}C) MHz, respectively, using the deuterium signal of the solvent as the lock and TMS as internal standard. The most important measurement parameters were as follows: sweep width 5 and 15 or 5 kHz, pulse width 1 and 7 or 3.5 μs ($\sim 20°$ and $\sim 80°$ or $\sim 30°$ flip angle), acquisition time 1.64 and 1.02 or 1.64 s, number of scans 4–16 and 1–100 K, computer memory 16 and 32 or 16 K. Complete proton noise decoupling (~ 3 or ~ 1.5 *W*) for the ^{13}C spectra and Lorentzian exponential multiplication for signal-to-noise enhancement were used (line width 0.7 and 1.0 or 2.0 Hz).

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