Proton magnetic resonance spectra of substituted phenylferrocenes Transmission of the substituent effect into the particular positions in ferrocene and some metallocenes

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The p.m.r. spectra of 29 phenylferrocenes were recorded. Hammett's correlations δ_α, δ_β, $\delta_{1'}$ *vs.* σ^0 constants of substituents and $\delta = \varrho_I\sigma_I + \varrho_R\sigma_R$ were made with phenylferrocenes, substituted ferrocenes, cations of benzenecyclopentadienyl iron, cobalticinium salts, and substituted cymantrenes. The transmission of the substituent effects into the particular positions in ferrocene and further metallocenes is discussed.

Были измерены спектры ПМР 29 фенилферроценов. Далее осуществили корреляция Гамметта δ_α, δ_β, $\delta_{1'}$ с σ^0 константами заместителей, а также корреляция $\delta = \varrho_I\sigma_I + \varrho_R\sigma_R$. Аналогичные сравнения производились и для замещенных ферроценов, катионов циклопентадиенилбензолжелеза, кобальтициния и замещенных цимантренов. Обсуждается перенос эффектов заместителя в отдельные положения в ферроцене, а также и в других металлоценах.

The transmission of the substituent effect in ferrocene has been studied in detail [1—6]. Some quantification has been attained when examining the p.m.r. spectra of substituted ferrocenes and arylferrocenes: the value of transmission into position 1' has been found to be 22 and 14%, respectively [7]. The cited authors assumed that the transmission through cyclopentadienyl iron (C_5H_5Fe) equals that of *p*-phenylene group. *Sato et al.* [8] investigated the p.m.r. spectra of 1'- and 2-substituted methylferrocenes in a similar way and also found that the substituent effect is transmitted through the ferrocene system almost equally well as through the *p*-phenylene group (transmission coefficients 0.28 and 0.37, respectively).

Shielding effects of substituents on the α, β, or 1' positions of substituted ferrocenes were studied by several authors; most of attention was paid to this problem by *Dvoryantseva et al.* [9, 10] and *Slocum* [11, 12].

The aim of this study was to estimate the coefficient of the transmission effect of the substituent to the particular positions of ferrocene and ascertain whether the inductive and resonance effects are equally well transmitted to all positions.

Experimental

Arylferrocenes were prepared by arylation of ferrocene by the properly substituted benzenediazonium salts excepting (3-ethylphenyl)- and (4-ethylphenyl)ferrocene, which were obtained by $LiAlH_4(AlCl_3)$ reduction of the particular acetyl derivatives [13].

The p.m.r. spectra of 3—8% deuteriochloroform solutions (99.5% D isotope) were measured using a Tesla 487 apparatus at 80 MHz and 23°C and recorded on δ scale in p.p.m. units. Tetramethylsilane was used as an internal standard. The reading accuracy of chemical shifts was ± 0.01 p.p.m. They are listed in Table 1 and were ascribed according to [6]. Unapproximated statistical relations were used for correlations using the digital computer Gier. In these calculations σ^0 constants according to [14] were applied. The σ_I and σ_R were adopted from [15] and [16].

Results and discussion

Three types of signals, associated with protons of ferrocene ring, are characteristic of all arylferrocene spectra under investigation. Singlet at about 4.0δ belongs to protons of the unsubstituted cyclopentadienyl ring (1' protons); protons located in positions 2 and 5 of the substituted ring (α protons) absorb as an apparent triplet at about 4.6δ. The apparent triplet of β protons (positions 3 and 4 of the substituted ring) is in the 4.3δ region. The shape of triplets of α and β protons and also the difference in their chemical shifts depend on the character of substituent. The greatest difference in their chemical shifts was observed with m-trifluoromethylphenyl ferrocene — up to 0.4δ. The multiplet of protons of the substituted phenyl lies within the $6.5—8.0\delta$ region.

A relative good correlation of δ_α and δ_β ($r > 0.9$, see Table 2) was achieved without the twice substituted derivatives, i.e. the correlation was taken of 25 derivatives. The correlation of chemical shifts of protons of the unsubstituted cyclopentadienyl ring ($\delta_{1'}$) vs. $\sigma^0_{p,m}$ constants is much worse, since the chemical shift is little substituent dependent. It could be said that phenyl substituents exert almost an equal effect both on the α and β positions of ferrocene ($\varrho_\beta/\varrho_\alpha = 0.96$). Position 1' is affected by the phenyl substituents to a minor extend only ($\varrho_{1'}/\varrho_\beta = 0.12$, $\varrho_{1'}/\varrho_\alpha = 0.12$). Our results are very close to those presented by *Butter* [7].

The effect of substituents, directly bounded to cyclopentadienyl ring of ferrocene (II), on individual positions of ferrocene had to be recalculated though we made use of data reported by *Dvoryantseva et al.* [9]; the authors ascribed chemical shifts of H_α and H_β for $-NH_2$ and $-OCH_3$ derivatives inversely as was proved by *Slocum* [12]. Moreover, Dvoryantseva used for correlations of chemical shift of various protons various σ constants, so that a direct comparison was impossible. Good correlations of δ_α and δ_β vs. σ^0_p constants were achieved ($r \doteq 0.95$, see Table 3). This means that both resonance and inductive effects of substituents are transmitted into α and β positions. Comparison of ϱ_β and ϱ_α evidences that the substituent effect on α position is more pronounced ($\varrho_\beta/\varrho_\alpha = 0.80$).

The correlation $\delta_{1'}$ vs. σ^0_p is relatively worse ($r \sim 0.9$). *Dvoryantseva* [9] reported much better correlations against σ_i constants ($r = 0.98$) what means that the resonance effects of substituents are not transmitted from the other ring into position 1'

Table 1

Chemical shifts of cyclopentadienyl protons of substituted phenylferrocenes (I)

No.	X	δ_1'	δ_α	δ_β
1	H	4.027	4.625	4.286
2	4-N(CH$_3$)$_2$	4.022	4.541	4.218
3	4-OH	4.030	4.556	4.260
4	4-OCH$_3$	4.021	4.558	4.246
5	4-C$_2$H$_5$	4.020	4.588	4.254
6	4-CH$_3$	4.020	4.593	4.260
7	4-Cl	4.020	4.588	4.298
8	4-Br	4.020	4.586	4.298
9	4-COOC$_2$H$_5$	4.010	4.668	4.358
10	4-COCH$_3$	4.032	4.690	4.365
11	4-CHO	4.035	4.700	4.415
12	4-CN	4.027	4.676	4.406
13	4-SO$_2$CH$_3$	4.048	4.718	4.428
14	4-NO$_2$	4.050	4.738	4.464
15	3-C$_2$H$_5$	4.025	4.606	4.273
16	3-CH$_3$	4.030	4.608	4.274
17	3-OCH$_3$	4.036	4.615	4.283
18	3-OH	4.030	4.594	4.283
19	3-COCH$_3$	4.025	4.681	4.334
20	3-Cl	4.040	4.658	4.348
21	3-Br	4.044	4.605	4.319
22	3-CHO	4.035	4.695	4.359
23	3-CF$_3$	4.122	4.738	4.321
24	3-NO$_2$	4.050	4.706	4.395
25	3,4-di-CH$_3$	4.020	4.575	4.248
26	3,5-di-CH$_3$	4.022	4.575	4.250
27	3-OCH$_3$-4-COCH$_3$	4.038	4.676	4.378
28	3,4-di-Cl	4.035	4.583	4.333
29	3-CF$_3$-4-Cl	4.106	4.626	4.366

Table 2

Results of correlation analysis for substituted phenylferrocenes (I)

	Type of constant	ϱ	Number of derivatives	S_ϱ	S_r	Not correlated derivatives
δ_α	$\sigma_{p,m}^0$	0.1303	28	0.7868	0.0200	0.0375	
	$\sigma_{p,m}^0$	0.1585	25	0.9248	0.0136	0.0238	3,4-Cl, Cl; 3,4-CF$_3$, Cl; 4-Br
δ_β		0.1446	28	0.8681	0.0162	0.0304	
		0.1527	25	0.9189	0.0137	0.0230	3,4-CH$_3$, CH$_3$; 3,5-CH$_3$, CH$_3$; 4-NO$_2$
δ_1'	$\sigma_{p,m}^0$	0.0183	26	0.6036	0.0049	0.0088	3-CF$_3$; 3,4-CF$_3$, Cl
	$\sigma_{p,m}^0$	0.0194	23	0.7595	0.0037	0.0065	4-COOC$_2$H$_5$; 3-COCH$_3$; 4-Br

To be able to calculate the transmission coefficients to position 1′ we had to use, as was the case with arylferrocenes, the same, *i.e.* the σ_p^0 constants. As it follows from values $\varrho_{1'}/\varrho_\alpha = 0.28$, or $\varrho_{1'}/\varrho_\beta \doteq 0.35$, transmission of the substituent effect through cyclopentadienyl iron (C_5H_5Fe) is approximately the same as through the *p*-phenylene group ($\pi' = 0.37$) [17].
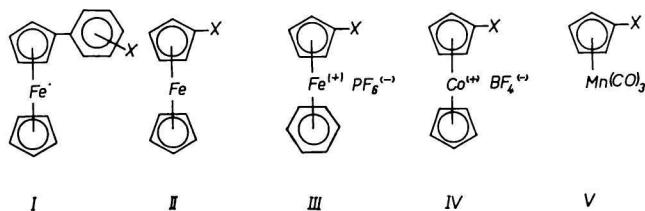
I. X = see Table 1;
II. X = H, C_2H_5, NH_2, OCH_3, $OCOCH_3$, Cl, Br, I, $COCH_3$, CN, NO_2;
III. X = H, C_2H_5, NH_2, OCH_3, $COCH_3$, Cl, COOH, $NHCOCH_3$, $N(CH_3)_2$, OC_2H_5, SC_6H_5;
IV. X = H, NH_2, NO_2, $COOCH_3$, CH_3, COOH;
V. X = H, CH_3, CHO, COOH, $COCH_3$, $NHCOCH_3$.

Scheme 1

Comparison of data for substituted phenylferrocenes with those for substituted ferrocenes suggested that the increased distance of a substituent lowers the difference between influencing α and β positions in ferrocene and the diversity of position 1′ becomes more significant. Inserting of phenyl between the substituent and ferrocene is manifested more markedly on $\varrho_{1'}$ than on ϱ_α or ϱ_β.

Chemical shifts of α and β protons of the substituted cyclopentadienyl ring of the cations of benzene cyclopentadienyl iron (*III*) [18], cobalticinium (*IV*) [19], and cymantrene (*V*) [20] (cyclopentadienylmanganese tricarbonyl [21]) was correlated *vs.* σ_p^0 constants. The chemical shifts of groups bounded through an atom with a free electron pair to the cyclopentadienyl ring in benzene cyclopentadienyl iron were ascribed analogously as did *Slocum* and *Ernst* with ferrocenes [12]; generally, the chemical shift of α protons is more downfield shifted than that of β protons.

As seen from data listed in Table 4, the α position is always more sensitive to the substituent effects than β position, analogously as is the case with ferrocenes or phenylferrocenes. The ratio $\varrho_\beta/\varrho_\alpha$ varies markedly from 0.80 through 0.52 to 0.44. Considering the small number of derivatives it is quite difficult to presume to which extent this change is caused only by the character of the central atom (metal). From the data obtained for substituted ferrocenes and derivatives of cation of benzene cyclopentadienyl iron it follows that there is no substantial difference between a neutral molecule and an ion.

A two-parameter regress analysis was undertaken to find out to which extent the inductive and resonance effects of substituents are transmitted into the particular $(\alpha, \beta, 1')$ positions of ferrocene and phenylferrocenes of the benzene cyclopentadienyl iron cation, cobalticinium, and cymantrene (α, β). The correlations $\delta = \varrho_I \sigma_I + \varrho_R \sigma_R$ offered statistically more significant results than those according to Yukawa—Tsuno equation. Results are listed in Table 5.

To obtain precise results it is necessary to have a greater number of experimental data [15]; our results allow only qualitative conclusions to be made. The resonance effect of substituents is transmitted approximately equally both to α and β positions of the substituted cyclopentadienyl ring. It could be said that the character of the atom of metal, as well as ligands bound to it is relatively little reflected on the ϱ_R if we do not consider phenylferrocenes, which reveal low correlation coefficients. The character of the metal is substantially reflected on the ϱ_I values; the inductive effect of substituents is much better transmitted into α than in β position.

Table 3

Results of correlation analysis for substituted ferrocenes (*II*)

Type of constant	Number of derivatives			S_r	S_ϱ	Not correlated derivatives
δ_α	12	0.9493	1.0597	0.1278	0.1109	
	9	0.9781	0.7996	0.0571	0.0643	—NO$_2$, —COOCH$_3$, —COCH$_3$
δ_β	12	0.8521	0.5960	0.1335	0.1158	
	9	0.9557	0.6448	0.0842	0.0751	—OCOCH$_3$, —Cl, —H
$\delta_{1'}$	12	0.8612	0.2746	0.0591	0.0513	
	9	0.9092	0.2255	0.0381	0.0390	—C$_2$H$_5$, —CN, —COCH$_3$

Table 4

Correlation analysis of metallocenes (*III — V*)

Type of compound	Number of points	Type of hydrogen	Type of constant	Correlation coefficient	ϱ	S_r	S_ϱ
III	10	α		0.931	0.889	0.105	0.123
	10	β		0.928	0.712	0.086	0.101
IV	5	α		0.951	0.960	0.206	0.222
	5	β		0.736	0.507	0.306	0.330
V	5	α		0.993	1.489	0.614	0.102
	5	β		0.937	0.659	0.086	0.142

Table 5

Two-parameter correlation analysis for metallocenes $(I-V)$

Type of compound	Number of points	Type of hydrogen	Multiple correlation coefficient		ϱ_R	$S_{\varrho I}$	$S_{\varrho R}$	Mean deviation	F value
I	23	α	0.874	0.113	0.216	0.049	0.016	0.028	32.460
	23	β	0.908	0.164	0.186	0.041	0.097	0.024	47.391
II	12	α	0.940	1.160	1.084	0.077	0.066	0.021	34.338
	12	β	0.953	0.344	0.981	0.164	0.140	0.045	44.656
	12	$1'$	0.911	0.429	0.144	0.077	0.066	0.021	21.821
III	10	α	0.947	1.051	0.820	0.181	0.098	0.045	30.222
	10	β	0.985	0.296	0.860	0.093	0.050	0.023	117.986
IV	6	α	0.896	0.665	1.070	0.218	0.419	0.105	4.060
	6	β	0.886	−0.246	1.197	0.252	0.485	0.122	3.657
V	6	α	0.976	1.459	1.096	0.244	0.255	0.084	30.158
	6	β	0.977	0.230	0.907	0.174	0.181	0.060	32.393

The analysis showed that the cyclopentadienyl ring (if it is a ligand in a transition metal organometallic compound) does not possess any position analogous to the *m*-position of benzene. The α position is comparable with *o*-position and β positions with *p*-position of benzene.

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Translated by Z. Votický