^{13}C NMR SPECTRA OF 1-ARYL-FERROCENYLETHYLENES

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^{13}C NMR spectra of 18 ferrocene analogues of *trans* stilbenes (1-aryl-2-ferrocenylethylenes) were measured. It was found that bridge group weakens the transfer of the substituent electron effects into ferrocene nucleus, especially distinctly into 3′,4′positions of cyclopentadienyl ring. The transfer of substituent effects into β-position of the bridge —CH=CH— is greater in derivatives studied by us than that in stilbenes. Synthesis of 1-(4-dimethylaminophenyl)-2-ferrocenylethylene is described.

In our previous papers we have systematically studied by means of ^{13}C NMR spectroscopy the transfer of substituent effects into various positions of the ferrocene skeleton in arylferrocenes[1] and in ferrocene analogues of chalcones[2]. In the last case we have directed our attention also to the influence of the substituent effects on chemical shifts of carbon atoms of the bridge —CO—CH=CH—. The influence of electron substituent effects on chemical shifts of carbon atoms in benzoylferrocenes was discussed by Roberts[3], who lately studied also arylferrocenes[4]. ^{13}C NMR spectra of substituted stilbenes were studied by Christoforou[5].

The aim of this work was to measure ^{13}C NMR spectra of ferrocene analogues of stilbenes and to study the influence of the bridge —CH=CH— on the transfer of electron substituent effects into the particular positions of ferrocene and the comparison of these effects with those in analogous derivatives of stilbene.

EXPERIMENTAL

^{13}C NMR spectra were recorded on spectrometer JEOL FX-100 at 25·05 MHz, with proton decoupling. The samples were measured as 10% and saturated solutions in C^2HCl_3, resp., at ambient temperature. The signal of deuterium was used as internal lock. The repetition of pulses was 3·6 s. The chemical shifts were determined relatively to internal standard tetramethylsilane, with the accuracy ±1 Hz.

Preparation of 1-(4-dimethylaminophenyl)-2-ferrocenylethylene: To the stirred solution of 0·3 g (9 mmol) 1-(4-aminophenyl)-2-ferrocenylethylene, 0·34 g (19 mmol) formaldehyde and 2·7 ml of alcoholic solution of KOH (concentration 1 mol dm^{-3}) in 5 ml of ethanol saturated with CO, 0·25 ml (18 mmol) Fe(CO)$_5$ was added at reflux. The reaction mixture was heated for

5 h. After this time no presence of starting compound was detected by means of TLC. After acidification with 3 ml 35% HCl was the solvent evaporated and 3 g NaHCO$_3$ were added to the residual. The tar impurities were removed from the precipitated solid material by two extractions with ether. The residue was extracted with dichloromethane. After evaporation of the solvent, the rest was chromatographed on Al$_2$O$_3$ column, with benzene as eluent. 0·28 g (85%) of red--orange needles was obtained. Melting point, after crystallization from mixture acetone–hexane, was 166—167·5°C. For C$_{20}$H$_{21}$FeN (331·2) calculated: 72·52% C, 6·39% H, 16·86 % Fe, 4·23% N; found: 72·56% C, 6·50% H, 16·04% Fe, 4·27% N.

RESULTS AND DISCUSSION

The ferrocene analogues of stilbenes, required for our study, were prepared either by acylation of ferrocene by chlorides of substituted phenylacetic acids and subsequent reduction of obtained phenylacylferrocenes and elimination of water, or by Wittig's reaction and they were described earlier[6]. In the mentioned paper the synthesis of 1-(4-dimethylaminophenyl)-2-ferrocenylethylene was not described, while the classic methylations of 1-(4-aminophenyl)-2-ferrocenylethylene by treatment with iodomethane or dimethyl sulfate, resp., were unsuccesful. The suitable method of preparation has proved to be the reductive methylation of amino derivative by formaldehyde and potassium hydridotetracarbonylferrit [KHFe(CO)$_4$]. Using this method, the required derivative was prepared in 85% yield.

^{13}C NMR chemical shifts of studied *trans* derivatives of ferrocene analogues of stilbenes are presented in Table I. From the dependence of chemical shifts on substituents, it is obvious that similarly as with stilbenes, the alternation of the polarization of carbon atoms of double bond and those of cyclopentadienyl ring is observed. This is true with the exception of cases when both C$_{(2',5')}$ and C$_{(3',4')}$ carbon atoms of cyclopentadienyl ring have the same polarization. The fact that electron acceptor substituents shift the chemical shifts to the downfield is described in the formula *I* by sign +, the opposite effect by − sign.
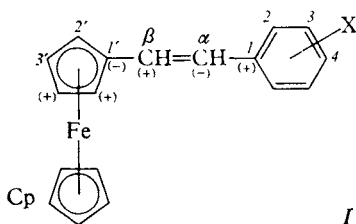

I

This fact can be seen even more distinctly from Table II, where the results of one parameter Hammett's correlation[7] are presented. Correlations of chemical shifts of C$_{(1)}$ and C$_{(\alpha)}$ are biased with a great error. This is reflected in lower values of correlation coefficients as well as in great standard deviations. Chemical shifts of un-

TABLE I
^{13}C Chemical shifts of 1-aryl-2-ferrocenylethylenes

X	$C_{(\alpha)}$	$C_{(\beta)}$	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	$C_{(6)}$	$C_{(1')}$	$C_{(2')}$	$C_{(3')}$	$C_{(Cp)}$[a]	Other
H	126·01	126·84	137·83	125·74	128·57	126·72	—	—	83·37	66·84	69·01	69·21	—
4-N(CH₃)₂	126·24	122·28	126·24	126·70	112·66	149·63	—	—	84·53	66·34	68·49	69·07	40·54
4-NH₂	126·14	122·98	128·30	126·90	115·25	145·38	—	—	84·25	66·46	68·58	69·09	—
4-OCH₃	125·62	124·50	130·69	125·62	114·05	158·64	—	—	83·93	66·58	68·74	69·13	55·24
4-OC₂H₅	125·69	124·40	130·57	126·86	114·63	158·03	—	—	83·95	66·55	68·72	69·13	63·41 14.84
4-CH₃	125·72	125·94	135·05	125·62	129·28	136·44	—	—	83·56	66·70	68·84	69·11	21·18
4-C₂H₅	125·79	125·99	135·34	125·74	128·11	135·44	—	—	83·63	66·72	68·87	69·16	28·58 15.57
4-F[b]	124·82	126·63	134·06	127·12	115·13	161·77	—	—	83·22	66·79	69·01	69·18	—
4-Cl	124·72	127·72	136·37	126·91	128·74	126·79	—	—	83·10	66·97	69·30	69·30	—
4-CHO	124·56	131·52	144·04	126·08	130·35	134·62	—	—	82·26	67·34	69·74	69·39	191·54
4-CN	123·84	131·59	142·31	125·94	132·37	109·37	—	—	81·83	67·31	69·74	69·30	119·26
4-NO₂	123·45	132·91	144·41	125·89	124·23	145·97	—	—	81·78	67·50	70·04	69·45	—
3-CH₃	126·06	126·38	137·71	126·55	137·98	128·45	127·52	122·92	83·37	66·77	68·89	69·13	21·40
3-OCH₃	125·96	127·31	139·36	111·16	159·95	112·45	129·59	118·53	83·31	66·93	69·09	69·27	55·29
3-F[c]	124·77	128·52	140·27	111·99	163·26	113·44	129·98	121·67	82·78	67·04	69·30	69·30	—
3-Cl	124·40	128·62	139·76	125·45	134·56	126·52	129·76	123·96	82·63	66·99	69·23	69·23	—
3-Br	124·48	129·45	140·13	128·62	124·33	130·08	128·62	125·74	82·50	67·01	69·21	69·21	—
3-NO₂	123·21	131·40	139·59	119·93	148·72	120·99	129·41	130·58	81·91	67·22	69·56	69·27	—

[a] Cp unsubstituted cyclopentadienyl ring; [b] coupling constants in Hz, $^{1}J(CF) = 246$, $^{2}J(CF) = 21·4$, $^{3}J(CF) = 7·9$, $^{4}J(CF) = 7·9$, $^{5}J(CF) = 1·8$; [c] coupling constants in Hz, $^{1}J(CF) = 244·8$, $^{2}J(CF) = 21·7$, $^{3}J(CF) = 7·9$, $^{4}J(CF) = 2·4$.

substituted Cp ring atoms are practically independent of substituents. The correlations of chemical shifts of $C_{(2',5')}$ and $C_{(3',4')}$ atoms of ferrocene skeleton were substantially improved, when the correlation was carried out with σ_p^- constants of substituents (Table II). This reflects the fact that iron atom in ferrocene can well stabilize the neighbouring positive charge[8,9]. The same effect, which was indirectly pointed at by Roberts[4], can be found also in arylferrocenes, where the direct interaction of electron acceptor groups having $-M$ effect with cylopentadienyl ring is also possible. The correlations at ferrocene analogues of stilbenes as well as at arylferrocenes were distinctly improved by using σ_p^- constants of substituents. The structure of derivatives with strong electron acceptor groups can be well approximated by a canonical formula *II*.

II
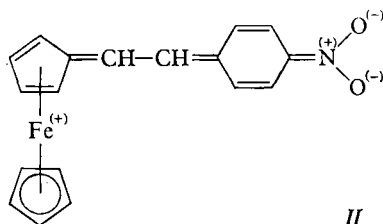
The possibility of some degree of polarization of the group —CH=CH— is supported by non-equivalency of chemical shifts of the basic derivative ($\Delta\delta = 0.83$). From the comparison of slopes of correlation of chemical shifts of atoms $C_{(1')}$,

TABLE II

The results of correlations of chemical shifts of 1-aryl-2-ferrocenylethylenes with σ constants[a]

Atom[a]	Constants	δ_o^{b}	ϱ^{c}	r^{d}	s.d.[e]
$C_{(1)}$	σ	135·44	11·413	0·918	2·129
$C_{(\alpha)}$	σ	125·33	−2·088	0·910	0·411
$C_{(\beta)}$	σ	126·66	7·143	0·985	0·535
$C_{(1')}$	σ	83·34	−1·956	0·991	0·114
$C_{(2',5')}$	σ	66·81	0·736	0·973	0·075
$C_{(3',4')}$	σ	69·02	0·979	0·960	0·123
$C_{(2',5')}$	σ_p^-	66·80	0·565	0·991	0·043
$C_{(3',4')}$	σ_p^-	69·01	0·759	0·988	0·068

[a] The number of derivatives in all correlations was 18; [b] δ_o the intercept; [c] ϱ the slope of the linear correlation $\delta = \delta_o + \varrho\sigma$; [d] r the correlation coefficient; [e] s.d. the standard deviation.

TABLE III

The results of correlations of chemical shifts of several derivatives of ferrocene and benzene with σ constants

Atom	$\varrho/r(n)$[a]				
	Fc—Ar[b]	Fc—CO—CH=CH—Ar	Fc—CH=CH—Ar	Fc—CO—Ar	C_6H_5—CH=CH—Ar
$C_{(\alpha)}$	—	—2·53/0·939(13)	—2·09/0·910(18)	—	—2·00/0·835(27)
$C_{(\beta)}$	—	5·03/0·990(13)	7·14/0·985(18)	—	5·44/0·986(27)
$C_{(1')}$	—3·22/0·948(17)	—0·63/0·986(13)	—1·96/0·991(18)	—	—1·37/0·988(27)
$C_{(2',5')}$	0·87/0·907(17)	0·17/0·953(13)	0·74/0·973(18)	—0·17/0·963(8)	—
$C_{(3',4')}$	1·65/0·927(17)	0·72/0·984(13)	0·98/0·960(18)	0·82/0·988(8)	—

[a] ϱ The slope of linear correlation, r the correlation coefficient, n the number of data in correlation; [b] Fc ferrocenyl, Ar aryl.

$C_{(2',5')}$ and $C_{(3',4')}$ in arylferrocenes, ferrocene analogues of chalcones and stilbenes, and benzoylferrocenes with σ constants of substituents (Table III), it is obvious that every bridge, i.e. —CO—CH=CH—, —CH=CH—, and also —CO—, weakens the transfer of substituent electron effects into the mentioned positions. The transfer is inhibited the least by ethylidene group. This can be very distinctly seen in the $C_{(2',5')}$ and can be explained by the coplanarity of the whole system. In ferrocene analogues of chalcones and in benzoylferrocenes it was proved that their system is not coplanar and nonbonded interaction of $H_{(2',5')}$ of cyclopentadienyl ring with H_{ortho} of benzene ring can occur. From the comparison of slopes of correlations of chemical shifts of bridge carbon atoms of stilbenes and their ferrocene analogues, it can be concluded that transfer of substituent effects into α-position is nearly the same in all of them, but the transfer into β-position is substantially better in ferrocene analogues of stilbenes. This can be explained by the hypothesis that the coplanarity of the whole system is possible due to the suitable geometry of cyclopentadienyl ring (dihedral angle of neighbouring C—H bonds being 150°), while in the case of stilbenes the distortion from the coplanarity of unsubstituted ring and the bridge —CH=CH— occurs.

We have also carried out two parameter correlations (Table IV). It can be concluded therefrom that in the para substituted derivatives all chemical shifts of ferrocene as well as ethylene carbon atoms, with the exception of $C_{(\alpha)}$, are more sensitive to resonance effects of substituents. This is in agreement with the values for stilbenes[5]. In meta substituted derivatives all chemical shifts are, as awaited, substantially more sensitive to inductive effects of substituents.

TABLE IV

The results of two parameter correlations of chemical shifts of 1-aryl-2-ferrocenylethylenes with σ_I and σ_R^0 substitutent constants[10]

Atom	para-Series[a]				meta-Series[b]			
	$\varrho_I{}^c$	$\varrho_R{}^c$	r	s.d.	$\varrho_I{}^c$	$\varrho_R{}^c$	r	s.d.
$C_{(\alpha)}$	−3·119	−1·858	0·988	0·182	−3·913	−1·965	0·996	0·112
$C_{(\beta)}$	5·691	10·924	0·985	0·512	6·232	3·064	0·987	0·343
$C_{(1')}$	−1·774	−2·667	0·993	0·126	−1·977	−1·048	0·995	0·066
$C_{(2',5')}$	0·622	1·152	0·990	0·063	0·553	0·137	0·968	0·045
$C_{(3',4')}$	0·998	1·449	0·983	0·111	0·806	0·264	0·966	0·069

[a] The number of derivatives in the correlation was 10; [b] the number of derivatives in the correlation was 7; [c] ϱ_I and ϱ_R the coefficients of the correlation $\delta_x = \delta_0 + \varrho_I\sigma_I + \varrho_R\sigma_R^0$.

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Translated by J. Koudelka.