

SUBSTITUENT EFFECT ON WAVE NUMBERS OF C=O VALENCE VIBRATIONS IN FERROCENE DERIVATIVES*

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Wave numbers of C=O valence vibrations of 83 ferrocene derivatives have been measured in tetrachloromethane. For a series of 154 compounds containing ferrocene skeleton linear correlation has been found between wave numbers of C=O vibration and $X^+(\text{R})$ constants of structural fragments in the sense of modified and extended Seth-Paul-Van Duyse equation. Validity has been verified of the recently derived empirical relation for calculation of the $X^+(\text{R})$ constants of complex structural fragments from values of constants of substituents and transmission factors for simple structural groupings. The transmission factors γ and π' for 1,3- and 1,1'-ferrocene system have been found to be well applicable to calculation of constants of structural fragments containing ferrocene skeleton.

Our previous papers¹⁻⁵ dealt with application of the modified and extended Seth-Paul-Van Duyse equation⁶ to various series of organic compounds containing one C=O bond or 1,3-dicarbonyl system. In the context of further studies in this field, we derived⁷ a general empirical formula enabling calculation of $X^+(\text{R})$ constants of complex structural fragments for the constants and transmission factors of electronic effects of simple structural groupings. A number of papers⁸⁻¹¹ were devoted to investigation of substituent effects on wave numbers of C=O valence vibrations in several series of ferrocene derivatives. Simple Hammett plots with σ or σ^+ constants as well as two-parameter equation by Yukawa and Tsuno were used for this purpose.

The aim of this communication was to measure – under identical standard conditions (in CCl_4) – wave numbers of C=O valence vibrations of further ferrocene derivatives and to verify validity of the modified and extended Seth-Paul-Van Duyse equation for these compounds.

EXPERIMENTAL

Synthesis as well as some chemical and physical properties of the compounds used in the spectral measurements were described¹²⁻²⁴.

* Part VII in the series On Application of Seth-Paul-Van Duyse Equation; Part VI: Chem. Zvesti, in press.

The wave numbers of C=O valence vibration were measured with a Zeiss Specord 75 IR and a Perkin-Elmer 567 spectrophotometers in CCl₄ solutions, using 1, 2.5, 5 and 10 mm cells. Concentration of the solutions was chosen to provide maximum absorption of 70–85% at the bands examined. The maxima of the absorption bands were read with the accuracy of $\pm 0.5 \text{ cm}^{-1}$. The wave number scale was calibrated according to reference spectrum of indene.

RESULTS AND DISCUSSION

Wave numbers are given of C=O valence vibration of compounds of general formula I,



where R¹ means structural fragments containing ferrocene skeleton (Table I). Using the values and relations published^{1,6,7} the respective constants X⁺(R¹) and X⁺(R²) were calculated for the two fragments R¹ and R², their sums are also given in Table I.

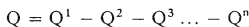
$$\sum X^+(R) = X^+(R^1) + X^+(R^2)$$

Detailed analysis of linear correlations type $\nu(\text{C}=\text{O})$ vs. σ^+ for many series of organic compounds²⁸ revealed that the constant used so far for the ferrocenyl residue, $\sigma_{\alpha}^+(\text{Fc}) = -1.55$, found by Hill and coworkers²⁹ does not reflect sufficiently accurately electronic effect of this group on wave number of C=O vibration. For this reason we used, for calculation of the X⁺(R) constant of the parent ferrocenyl fragment, the value $\sigma_{\alpha}^+(\text{Fc}) = -1.35$ found independently by Taylor and Ware²⁷ from kinetic and spectral measurements. Using Eq. (1) (ref.¹)

$$X^+(R) = 0.238\sigma^+(R) + 1.077 \quad (1)$$

we obtained the value X⁺(Fc) = 0.756 which was used in this paper instead of the earlier suggested¹ value X⁺(Fc) = 0.708. In similar way, X⁺(R) constant was calculated for 2-(1-methylpyrrol) residue, X⁺(2-(1-MePyrr)) = 0.584, from the value $\sigma_{\alpha}^+(2-(1-\text{MePyrr})) = -2.07$ taken from ref.³⁰.

For calculation of the X⁺(R) constants of complex structural fragments Q formed of a linear chain of *n* basic structural units Q¹



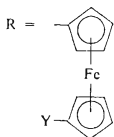
we used the general empirical relation (2) derived in ref.⁷

$$X^+(Q) = X^+(Q^1) + \gamma(Q^1) \delta^+(Q^2) + \sum_{i=3}^n \gamma(Q^{i-1}) \delta^+(Q^i) \prod_{j=1}^{i-2} \pi'(Q^j), \quad (2)$$

where γ and π' are transmission factors of electronic effects for the subfragments Q^i according to definition by Charton³¹ and Jaffé³², respectively, and the values $\delta^+(Q^i)$ are given by Eq. (3)

$$\delta^+(Q^i) = X^+(Q^i) - X^+(\text{Ph}). \quad (3)$$

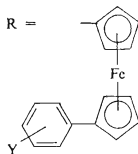
So *e.g.* according to Eq. (2) for the fragments type



it is

$$X^+(R) = X^+(\text{Fc}) + \gamma(1,1'\text{-Fc}) \delta^+(4\text{-Y}),$$

and for the fragments type



the $X^+(R)$ constant can be determined from the relation

$$X^+(R) = X^+(\text{Fc}) + \gamma(1,1'\text{-Fc}) \delta^+(4\text{-Ph}) + \pi'(1,1'\text{-Fc}) \delta^+(Y).$$

The constants of structural fragments $R = -\text{CH}=\text{CH}-\text{Y}$, where $\text{Y} = \text{Fc}$, heterocyclic residue or alkyl, can be calculated for *s-trans* and *s-cis* conformation of $\text{CH}=\text{CH}$ group, respectively, with respect to the examined $\text{C}=\text{O}$ bond from the following relations:

$$X^+(R)_{s\text{-trans}} = X^+(\text{CH}=\text{CH}_2)_{s\text{-trans}} + \gamma(\text{CH}=\text{CH})_{s\text{-trans}} \delta^+(4\text{-Y}),$$

$$X^+(R)_{s\text{-cis}} = X^+(\text{CH}=\text{CH}_2)_{s\text{-cis}} + \gamma(\text{CH}=\text{CH})_{s\text{-cis}} \delta^+(4\text{-Y}).$$

TABLE I

Wave numbers of C=O valence vibration (in cm^{-1}) and $\sum X^+(\text{R})$ values for compounds of general formula I

Compound No	R^1 ^a	R^2 ^a	$\nu(\text{C}=\text{O})^b$	$\sum X^+(\text{R})$
1	1'-PhFc	PhCH=CH (<i>s-cis</i>)	1 663	1-98
2	1'-(4-MePh)Fc	PhCH=CH (<i>s-cis</i>)	1 662.3	1-96
3	1'-(3-MePh)Fc	PhCH=CH (<i>s-cis</i>)	1 664	1-97
4	1'-(4-ClPh)Fc	PhCH=CH (<i>s-cis</i>)	1 663.6	1-98
5	1'-(3-ClPh)Fc	PhCH=CH (<i>s-cis</i>)	1 664	2-00
6	1'-(4-BrPh)Fc	PhCH=CH (<i>s-cis</i>)	1 663.4	1-99
7	1'-(3-BrPh)Fc	PhCH=CH (<i>s-cis</i>)	1 664.1	2-00
8	1'-(4-OMePh)Fc	PhCH=CH (<i>s-cis</i>)	1 662.7	1-93
9	1'-(3-CF ₃ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 664	2-01
10	1'-(4-NO ₂ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 664.9	2-02
11	1'-(3-NO ₂ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 663.6	2-02
12	1'-(3,4-Me ₂ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 663	1-95
13	1'-(3,5-Cl ₂ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 662.4	2-02
14	1'-(3,4-Cl ₂ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 663	2-01
15	1'-(3-CF ₃ , 4-ClPh)Fc	PhCH=CH (<i>s-cis</i>)	1 663	2-01
16	1'-(4-CO ₂ EtPh)Fc	PhCH=CH (<i>s-cis</i>)	1 662.9	2-01
17	1'-(4-OHPh)Fc	PhCH=CH (<i>s-cis</i>)	1 662.6	1-92
18	1'-COMeFc	4-MePhCH=CH (<i>s-cis</i>)	1 658	2-08
19	1'-COMeFc	3-BrPhCH=CH (<i>s-cis</i>)	1 662	2-21
20	1'-COMeFc	4-ClPhCH=CH (<i>s-cis</i>)	1 661	2-16
21	1'-COMeFc	4-BrPhCH=CH (<i>s-cis</i>)	1 661	2-16
22	1'-COMeFc	4-FPhCH=CH (<i>s-cis</i>)	1 661	2-12
23	1'-COMeFc	PhCH=CH (<i>s-cis</i>)	1 661	2-13
24	1'-COMeFc	3-OMePhCH=CH (<i>s-cis</i>)	1 661	2-15
25	1'-COMeFc	4-OMePhCH=CH (<i>s-cis</i>)	1 657	1-99
26	1'-COMeFc	4-CNPhCH=CH (<i>s-cis</i>)	1 663	2-26
27	Fc	4-NMe ₂ PhCH=CH (<i>s-cis</i>)	1 656 ^c	1-70
28	Fc	4-NH ₂ PhCH=CH (<i>s-cis</i>)	1 657.5 ^c	1-78
29	Fc	4-OMePhCH=CH (<i>s-cis</i>)	1 658 ^c	1-87
30	Fc	4-MePhCH=CH (<i>s-cis</i>)	1 658 ^c	1-96
31	Fc	PhCH=CH (<i>s-cis</i>)	1 660 ^c	2-01
32	Fc	4-FPhCH=CH (<i>s-cis</i>)	1 660.5 ^c	2-00
33	Fc	4-ClPhCH=CH (<i>s-cis</i>)	1 661 ^c	2-03
34	Fc	3-ClPhCH=CH (<i>s-cis</i>)	1 662 ^c	2-09
35	Fc	4-CNPhCH=CH (<i>s-cis</i>)	1 662.5 ^c	2-13
36	Fc	3-NO ₂ PhCH=CH (<i>s-cis</i>)	1 665.5 ^c	2-14
37	Fc	4-NO ₂ PhCH=CH (<i>s-cis</i>)	1 662.5 ^c	2-16
38	Fc	4-FcPhCH=CH (<i>s-cis</i>)	1 659.5	1-88
39	Fc	2-FuCH=CH (<i>s-cis</i>)	1 659	1-86
40	Fc	2-ThiCH=CH (<i>s-cis</i>)	1 657.5	1-90

TABLE I
 (Continued)

Compound No	R ^{1 a}	R ^{2 a}	$\nu(\text{C}=\text{O})^b$	$\sum X^+(\text{R})$
41	Fc	FcCH=CH (<i>s-cis</i>)	1 658	1.71
42	Fc	MeCH=CH (<i>s-cis</i>)	1 670	1.93
43	Fc	Me ₂ C=CH (<i>s-cis</i>)	1 659.5	1.78
44	FcCH=CH (<i>s-cis</i>)	4-NMe ₂ Ph	1 657 ^d	1.62
45	FcCH=CH (<i>s-cis</i>)	4-OMePh	1 660.5 ^d	1.84
46	FcCH=CH (<i>s-cis</i>)	4-MePh	1 662.5 ^d	1.96
47	FcCH=CH (<i>s-cis</i>)	Ph	1 665.5 ^d	2.02
48	FcCH=CH (<i>s-cis</i>)	4-FPh	1 664.5 ^d	2.01
49	FcCH=CH (<i>s-cis</i>)	3-OMePh	1 662 ^d	2.04
50	FcCH=CH (<i>s-cis</i>)	4-ClPh	1 663.5 ^d	2.06
51	FcCH=CH (<i>s-cis</i>)	4-BrPh	1 663 ^d	2.07
52	FcCH=CH (<i>s-cis</i>)	3-ClPh	1 664.5 ^d	2.12
53	FcCH=CH (<i>s-cis</i>)	3-BrPh	1 665 ^d	2.12
54	FcCH=CH (<i>s-cis</i>)	4-CNPh	1 664.5 ^d	2.19
55	FcCH=CH (<i>s-cis</i>)	3-NO ₂ Ph	1 666 ^d	2.19
56	FcCH=CH (<i>s-cis</i>)	4-NO ₂ Ph	1 666.5 ^d	2.22
57	FcCH=CH (<i>s-cis</i>)	Me	1 684 ^e	2.76
58	FcCH=CH (<i>s-cis</i>)	Et	1 688 ^e	2.71
59	FcCH=CH (<i>s-cis</i>)	Bu ⁱ	1 686 ^e	2.70
60	FcCH=CH (<i>s-cis</i>)	Pr ⁱ	1 658 ^e	2.66
61	FcCH=CH (<i>s-cis</i>)	2-(1-Me-Pyrr)	1 648	1.54
62	FcCH=CH (<i>s-cis</i>)	2-Fu	1 661.5	1.81
63	FcCH=CH (<i>s-cis</i>)	2-Thi	1 656	1.63
64	FcCH=CH (<i>s-trans</i>)	4-NMe ₂ Ph	1 633 ^d	1.14
65	FcCH=CH (<i>s-trans</i>)	4-OMe	1 637 ^d	1.35
66	FcCH=CH (<i>s-trans</i>)	4-MePh	1 638 ^d	1.47
67	FcCH=CH (<i>s-trans</i>)	Ph	1 640 ^d	1.53
68	FcCH=CH (<i>s-trans</i>)	4-FPh	1 641 ^d	1.52
69	FcCH=CH (<i>s-trans</i>)	3-OMePh	1 639 ^d	1.55
70	FcCH=CH (<i>s-trans</i>)	4-ClPh	1 642 ^d	1.57
71	FcCH=CH (<i>s-trans</i>)	4-BrPh	1 643 ^d	1.58
72	FcCH=CH (<i>s-trans</i>)	3-ClPh	1 643 ^d	1.64
73	FcCH=CH (<i>s-trans</i>)	3-BrPh	1 643 ^d	1.64
74	FcCH=CH (<i>s-trans</i>)	4-CNPh	1 645 ^d	1.70
75	FcCH=CH (<i>s-trans</i>)	3-NO ₂ Ph	1 645 ^d	1.70
76	FcCH=CH (<i>s-trans</i>)	4-NO ₂ Ph	1 646 ^d	1.73
77	FcCH=CH (<i>s-trans</i>)	Me	1 665 ^e	2.27
78	FcCH=CH (<i>s-trans</i>)	Et	1 663 ^e	2.22
79	FcCH=CH (<i>s-trans</i>)	Bu ⁱ	1 653 ^e	2.21
80	FcCH=CH (<i>s-trans</i>)	Pr ⁱ	1 663 ^e	2.17

TABLE I
 (Continued)

Compound No	R ^{1 a}	R ^{2 a}	$\nu(\text{C=O})^b$	$\sum X^+(\text{R})$
81	1'-COPhFc	4-NMe ₂ PhCH=CH (<i>s-cis</i>)	1 656 ^d	1.88
82	1'-COPhFc	4-NH ₂ PhCH=CH (<i>s-cis</i>)	1 659 ^d	1.90
83	1'-COPhFc	4-OMePhCH=CH (<i>s-cis</i>)	1 661 ^d	1.99
84	1'-COPhFc	4-MePhCH=CH (<i>s-cis</i>)	1 662 ^d	2.08
85	1'-COPhFc	PhCH=CH (<i>s-cis</i>)	1 665 ^d	2.13
86	1'-COPhFc	4-FPhCH=CH (<i>s-cis</i>)	1 665 ^d	2.12
87	1'-COPhFc	4-ClPhCH=CH (<i>s-cis</i>)	1 666 ^d	2.15
88	1'-COPhFc	4-CNPhCH=CH (<i>s-cis</i>)	1 667 ^d	2.25
89	1'-COPhFc	3-NO ₂ PhH=CH C(<i>s-cis</i>)	1 668 ^d	2.25
90	1'-COPhFc	4-NO ₂ PhCH=CH (<i>s-cis</i>)	1 669 ^d	2.28
91	1'-EtFc	MeO	1 721 ^f	3.47
92	1'-PrFc	MeO	1 721 ^f	3.47
93	1'-BuFc	MeO	1 721 ^f	3.47
94	1'-OMeFc	MeO	1 718 ^f	3.36
95	1'-CH ₂ PhFc	MeO	1 726 ^f	3.47
96	1'-CNFc	MeO	1 718 ^f	3.68
97	1'-CO ₂ MeFc	MeO	1 722 ^f	3.64
98	1'-BrFc	MeO	1 723 ^f	3.57
99	1'-COMeFc	MeO	1 726 ^f	3.65
100	1'-COEtFc	MeO	1 725 ^f	3.65
101	1'-COPrFc	MeO	1 725 ^f	3.65
102	1'-COPhFc	MeO	1 726 ^f	3.65
103	Fc	MeO	1 722 ^g	3.53
104	Fc	Cl(CH ₂) ₂	1 676 ^g	2.55
105	Fc	Cl(CH ₂) ₃	1 676 ^g	2.51
106	Fc	Ph	1 649 ^g	1.83
107	Fc	Br(CH ₂) ₂	1 679 ^g	2.53
108	Fc	HO	1 736 ^g	3.86
109	Fc	2-Fu	1 639 ^g	1.61
110	Fc	H	1 692 ^g	2.89
111	Fc	BrCH ₂ BrCH	1 683 ^g	2.66
112	Fc	PhCH ₂	1 670	2.43
113	Fc	Fc	1 640 ^g	1.51
114	Fc	2-Thi	1 639 ^g	1.44
115	Fc	ClCH ₂	1 689 ^g	2.77
116	Fc	Et	1 679.5	2.51
117	Fc	Me	1 677	2.56
118	1'-BrFc	Me	1 681	2.60
119	1'-ClFc	Me	1 680	2.59
120	1'-COPrFc	Me	1 686	2.69

TABLE I
(Continued)

Compound No	R ^{1 a}	R ^{2 a}	$\nu(\text{C}=\text{O})^b$	$\sum X^+(\text{R})$
121	1'-COPhFc	Me	1 686	2·68
122	1'-CH ₂ PhFc	Me	1 675	2·51
123	Fc(CH ₂) ₂	Me	1 725 ^g	3·54
124	4-FcPh	Me	1 684·5 ^h	2·72
125	3-FcPh	Me	1 690 ^h	2·88
126	2-FcPh	Me	1 690·2 ^h	2·65
127	Fc	CH ₂ =CH (<i>s-trans</i>)	1 664 ^g	1·54
128	Fc	CH ₂ =CH (<i>s-cis</i>)	1 671	2·09
129	1'-COMeFc	Ph	1 649	1·95
130	1'-COCH=CHPhFc (<i>s-cis</i>)	Me	1 679·5	2·69
131	1'-COEtFc	PhCH=CH (<i>s-cis</i>)	1 663	2·13
132	1'-COCH=CHPhFc (<i>s-cis</i>)	Et	1 682	2·64
133	1'-COPrFc	PhCH=CH (<i>s-cis</i>)	1 663	2·13
134	1'-COCH=CHPhFc (<i>s-cis</i>)	Pr	1 676	2·63
135	1'-COPr ⁱ Fc	PhCH=CH (<i>s-cis</i>)	1 663	2·13
136	1'-COCH=CHPhFc (<i>s-cis</i>)	Pr ⁱ	1 675·5	2·59
137	1'-CoPe ^{neo} Fc	PhCH=C (<i>s-cis</i>)	1 663	2·13
138	1'-COCH=CHPhFc (<i>s-cis</i>)	Pe ^{neo}	1 682	2·62
139	Fc	PhC≡C	1 633	1·41
140	1'-COMeFc	CH ₂ =CH (<i>s-cis</i>)	1 669	2·22
141	1'-COCH=CH ₂ Fc (<i>a-cis</i>)	Me	1 682	2·70
142	1'-COMeFc	MeCH=CH (<i>s-cis</i>)	1 672	2·06
143	1'-COCH=CHMeFc (<i>s-cis</i>)	Me	1 681	2·68
144	1'-COMeFc	Me ₂ C=CH (<i>s-cis</i>)	1 659·5	1·90
145	1'-COCH=CMe ₂ Fc (<i>s-cis</i>)	Me	1 681	2·66
146	4-[1'-(4-COMePh)Fc]Ph	4-ClPhCH=CH (<i>s-cis</i>)	1 665·5	2·03
147	1'-COMeFc	Ph	1 649	1·95
148	Fc	4-OMePhCH ₂	1 670·5	2·42
149	Fc	4-FPhCH ₂	1 672	2·43
150	1'-COCH ₂ PhFc	PhCH ₂	1 673	2·49
151	3-(4-OMePh)Fc	PhCH=CH (<i>s-cis</i>)	1 660·5	1·89
152	3-(4-MePh)Fc	PhCH=CH (<i>scis</i>)	1 661	1·93
153	3-(3-ClPh)Fc	PhCH=CH (<i>s-cis</i>)	1 661·5	1·99
154	3-(3-BrPh)Fc	PhCH=CH (<i>s-cis</i>)	1 662	1·99
155	3-(3-CF ₃ Ph)Fc	PhCH=CH (<i>s-cis</i>)	1 662·5	2·01
156	3-(4-OMePh)FcCH=CH (<i>s-cis</i>)	Ph	1 664·5	1·93
157	3-(3-MePh)FcCH=CH (<i>s-cis</i>)	Ph	1 665·5	1·98
158	3-(4-ClPh)FcCH=CH (<i>s-cis</i>)	Ph	1 666·5	1·99
159	3-(4-BrPh)FcCH=CH (<i>s-cis</i>)	Ph	1 666·5	2·00
160	3-(3-BrPh)FcCH=CH (<i>s-cis</i>)	Ph	1 667	2·01

TABLE I
(Continued)

Compound No	R ^{1a}	R ^{2a}	$\nu(\text{C}=\text{O})^b$	$\sum X^+(\text{R})$
161	3-(3-ClPh)FcCH=CH (<i>s-cis</i>)	Ph	1 666	2.01
162	3-(4-OMePh)FcCH=CH (<i>s-trans</i>)	Ph	1 642	1.43
163	3-(3-MePh)FcCH=CH (<i>s-trans</i>)	Ph	1 643.5	1.49
164	3-(4-ClPh)FcCH=CH (<i>s-trans</i>)	Ph	1 644.5	1.50
165	3-(4-BrPh)FcCH=CH (<i>s-trans</i>)	Ph	1 644.5	1.50
166	3-(3-BrPh)FcCH=CH (<i>s-trans</i>)	Ph	1 645.5	1.52
167	3-(3-ClPh)FcCH=CH (<i>s-trans</i>)	Ph	1 644.5	1.52

^a The abbreviations used in denoting the structural fragments R¹ and R²: Ph phenyl, Fc ferrocenyl, Me methyl, Fu furyl, Thi thienyl, Et ethyl, Buⁱ isobutyl, Prⁱ isopropyl, Pyrr pyrrol, Pr propyl, Bu butyl, Pe^{neo} neopentyl; (*s-cis*) and (*s-trans*) conformation of C=C bond with respect to the examined C=O bond or to C=O bond in the given structural fragment. ^b The wave numbers determined in this work except for the values denoted which were taken from literature. All the values were measured in CCl₄. ^c Taken from ref.⁸. ^d Taken from ref.⁹. ^e Taken from ref.²⁵ ^f Taken from ref.²⁶. ^g Taken from ref.¹. ^h Taken from ref.²⁷.

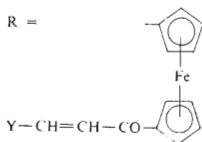
In analogous way X⁺(R) constants were obtained for two conformers of structural residues R = —CH=CH—C₆H₄X and for fragments R = —C≡C—C₆H₅:

$$\begin{aligned}
 X^+(\text{R})_{s\text{-trans}(s\text{-cis})} &= X^+(\text{CH}=\text{CH}_2)_{s\text{-trans}(s\text{-cis})} + \\
 &+ \gamma(\text{CH}=\text{CH})_{s\text{-trans}(s\text{-cis})} \delta^+(4\text{-Ph}) + \pi'(\text{CH}=\text{CH})_{s\text{-trans}(s\text{-cis})} \delta^+(\text{Y}), \\
 X^+(\text{R}) &= X^+(\text{C}\equiv\text{CH}) + \gamma(\text{C}\equiv\text{C}) \delta^+(4\text{-Ph}).
 \end{aligned}$$

In the case of the fragments type R = —CH=CY₂, approximate values of X⁺(R) constants were determined from the relation:

$$\begin{aligned}
 X^+(\text{R})_{s\text{-trans}(s\text{-cis})} &\cong X^+(\text{CH}=\text{CH}_2)_{s\text{-trans}(s\text{-cis})} + \\
 &+ \gamma(\text{CH}=\text{CH})_{s\text{-trans}(s\text{-cis})} 2\delta^+(4\text{-Y}).
 \end{aligned}$$

The constants of more complicated structural fragments containing ferrocene skeleton, carbonyl group, and CH=CH group:



were calculated from the following relation:

$$\begin{aligned} X^+(R) = & X^+(\text{Fc}) + \gamma(1,1'\text{-Fc}) \delta^+(4\text{-CHO}) + \\ & + \pi'(1,1'\text{-Fc}) \gamma(\text{CO}) \delta^+(4\text{-CH=CH}_2) + \\ & + \pi'(1,1'\text{-Fc}) \pi'(\text{CO}) \delta(\text{CH=CH}) \delta^+(4Y). \end{aligned}$$

The term $\delta^+(4\text{-Y})$ of the above-given formula was replaced by the term $2\delta^+(4\text{-Y})$ for the fragments type $1'-(\text{Y}_2\text{C=CHCO})\text{Fc}$.

For 1,3-substituted ferrocene derivatives the constants $X^+(R)$ were calculated by analogous relations to those used for 1,1'-isomers, the only difference being in using the transmission factors $\gamma(1,3\text{-Fc})$ and $\pi'(1,3\text{-Fc})$ instead of the values $\gamma(1,1'\text{-Fc})$ and $\pi'(1,1'\text{-Fc})$, respectively.

TABLE II

The $\delta^+(Q)$ values for some substituents Q in benzene nucleus

Q	$\delta^+(Q)$	$\sigma^+(Q)$
4-Pr	-0.062	-0.29 ^a
4-Bu	-0.062	-0.29 ^a
4-CH=CH ₂	0.031	0.10 ^a
2-Fc	~ -0.162 ^b	-0.71 ^c
4-COPh	0.128	0.51 ^d
4-COEt	~ 0.131 ^e	0.52 ^a
4-COPr	~ 0.131 ^e	0.52 ^a
4-Pr ⁱ	~ -0.060 ^f	-0.28 ^a
4-Pe ^{neo}	~ -0.060 ^f	-0.28 ^a
4-CH ₂ Ph	-0.057	-0.27 ^a

^a From ref.³³. ^b Determined approximately from $\sigma^+(4\text{-Fc})$. ^c From ref.²⁷. ^d From refs.^{34,35}.

^e Determined approximately from $\sigma^+(4\text{-COMe})$. ^f Determined approximately from $\sigma^+(4\text{-Pr})$.

For all the calculations the $X^+(R)$ and δ^+ constants as well as the γ and π' transmission factors were taken from refs^{1,6,7}. For some substituents, however, the $\delta^+(Q)$ values have not been published yet, so they were calculated from the respective σ^+ constants by Eqs (1) and (3). These values are given in Table II.

The value used for benzoyl group, $\delta^+(4\text{-COPh}) = 0.128$, was determined from $\sigma^+(4\text{-COPh}) = 0.51$ given by Titus and Fried³⁴ (from kinetic measurements) and by Nelson and coworkers³⁵ (from ¹⁹F NMR spectral data). It was shown²⁸ that the given value reflects better quantitative electronic effects of 4-COPh substituent on wave number of C=O valence vibrations than the previously suggested¹ constant obtained from the σ value taken from ref.³⁶.

Values of a series of 154 wave numbers of C=O valence vibrations of ferrocene derivatives *I* (Table I) measured in diluted solutions in CCl₄ give statistically significant correlation with the $\sum X^+(R)$ values according to the modified and extended Seth-Paul-Van Duyse equation (4),

$$\nu(\text{C=O}) = 37.47 (\pm 0.63) \sum X^+(R) + 1585.2 (\pm 15.4), \quad (4)$$

$$r = 0.984, \quad s = 0.56$$

where *r* and *s* stand for correlation coefficient and standard deviation, respectively. The dependence is represented in Fig. 1. The compounds No 41–44, 53, 62, 65, 79, 95, 129, 134, 142, and 147 were excluded from the correlation, since their deviation from linearity was greater than $\pm 5 \text{ cm}^{-1}$.

When comparing the relation (4) with the modified Seth-Paul-Van Duyse equation¹ (5) which is valid for a series of 439 values of wave numbers of C=O valence

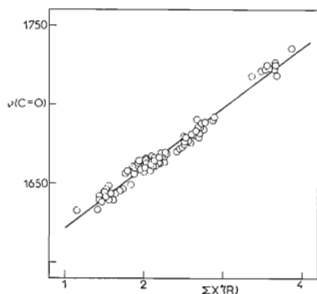


FIG. 1
Dependence $\nu(\text{C=O})$ vs $\sum X^+(R)$ for ferrocene derivatives *I*

vibrations of simple organic molecules,

$$\nu(\text{C}=\text{O}) = 38.22 (\pm 0.19) \sum X^+(\text{R}) + 1583.4 (\pm 12.7), \quad (5)$$

it is found that the parameters of the two correlations are practically identical (with respect to magnitude of their standard deviation).

Thus the modified and extended Seth-Paul-Van Duyse equation complies equally well with a number of compounds containing ferrocene skeleton and complex structural fragments. This fact also proves general validity of the earlier derived⁷ equation (2) for calculation of $X^+(\text{R})$ constants of complex structural fragments. In conclusion it can be stated, too, that the transmission factors γ and π' of electron effects determined¹¹ for 1,1'- and 1,3-ferrocene systems can be practically well applied to calculations of empirical constants expressing effects of complex structural groups with ferrocene skeleton.

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