

[G022]

DEPENDENCE OF SPECTRAL PARAMETERS IN ^1H AND ^{13}C NMR SPECTRA OF AROMATIC COMPOUNDS UPON SUBSTITUENT SPATIAL-STRUCTURAL PECULIARITIES

II. Investigation of the dependence of δ_i^{H} basic spectral parameters in NMR ^1H spectra of $\text{C}_6\text{H}_5\text{X}$ monosubstituted benzenes upon substituent constants σ

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Abstract

The dependences of differential spectral parameters ($\Delta\delta_i^{\text{H}}$) in spectra NMR ^1H of monosubstituted benzenes $\text{C}_6\text{H}_5\text{X}$ on substituent constants (σ) were investigated. The best correlation was founded for set of para-Brown's constants (σ^+).

Key words: NMR ^1H spectra of monosubstituted benzenes, basic (δ_i^{H}) and differential ($\Delta\delta_i^{\text{H}}$) spectral parameters, calculated average parameter of chemical shifts (CAP), substituent constants (σ), sets of constants (σ), $\Delta\delta_i^{\text{H}}-\sigma$ and $\Delta\text{CAP}-\sigma$ dependencies, correlation coefficient R, "linearity degree" of dependencies $\Delta\delta_i^{\text{H}}-\sigma$ and $\Delta\text{CAP}-\sigma$.

Introduction

Earlier we have published the data [1–3] about linear dependencies between basic spectral parameters of three types of aromatic protons (δ_i^{H}) in NMR ^1H spectra of monosubstituted benzenes $\text{C}_6\text{H}_5\text{X}$ and various constants (σ) characterizing the nature of substituent X. Among 32 investigated correlations the dependence of chemical shift of protons located in para-position to the substituent (δ_p^{H}) upon σ_p^+ Brown constants was the best one. Correlation coefficient R was 0,963.

The other two parameters (δ_o^{H} and δ_m^{H}) and suggested by us [1–3] calculated average parameter of chemical shifts (CAP) of all five protons in phenyl ring also directly depend upon different σ constants with worse correlation coefficient, indeed. This report deals with in-depth analysis of $\delta_i^{\text{H}}-\sigma$ and $\text{CAP}-\sigma$ dependencies.

Experimental Data

The accuracy of used values of δ_i^H (CAP) and σ parameters essentially affects the values of R coefficients characterizing the linearity of δ_i^H - σ and CAP- σ dependencies. Therefore selection principles for the present investigation are listed below.

Basic spectral parameters δ_i^H

In order to receive coordinated values of δ_i^H basic spectral parameters it is necessary to use data obtained in the same solvent. Moreover, it is desirable they would be taken from the same source of information. Internet-site [4] was such a source in paper [3]. The most of δ_i^H values were received using CDCl_3 solvent. NMR ^1H as well as ^{13}C spectra were studied by authors [4] for several decades and usually they well correlate with each other. However a part of data was received during initial period of investigations using low-frequency instruments (90 MHz) and was not renewed. Such NMR ^1H spectra had low resolution and often signals of two or even three types of aromatic protons (e.g. in alkylbenzenes) joined and formed wide multiplet. In such a case in previous works [1–3] we had to assume value of each parameter δ_o^H , δ_m^H and δ_p^H equal to δ_i^H value of the multiplet signal centre. Analyzing now well-resoluted spectra of these compounds we understand that the decision was wrong. Obviously we may await the improvement of correlation in spectra obtained using high-frequency instruments, where mentioned signals are sufficiently divided.

The defect connecting with bad signal resolution may be rectified using spectral data from the atlas produced by “Aldrich” firm [5] as a main source of information. Adduced NMR ^1H spectra of $\text{C}_6\text{H}_5\text{X}$ monosubstituted benzenes were received mostly (but not all of them) in deuteriochloroform using a high-frequency instrument (300 MHz). Their multiplet signals are overlapped in such degree that it is possible to determine the absorption centre of every three types of protons. The values of chemical shifts δ_i^H are given in [5] with the accuracy of 0.01 ppm but for all that authors do not give signals attribution in the spectra. Therefore we attributed orto-, metha- and para-protons absorption to the doublet and two triplets correspondingly. The latter one is twice less than the first one by its integral intensity. Values δ_i^H of the triplet central peaks are assumed as numerical values of δ_m^H and δ_p^H parameters but δ_o^H values for orto-protons equal to the average value between two doublet peaks. Hence in some cases δ_o^H values are given with the accuracy of 0,005 ppm but at calculations these values are rounded off to the nearest greater value divisible by 0,01 ppm.

Our signal attributions [5] in spectra we correlated with the similar ones given in [4]. Since it has been noted earlier [6] that the similar δ_i^H values from mentioned sources co-ordinate with each other, we also use δ_i^H values from [4].

We selected “representative set” of 25 functional groups X and unsubstituted benzene (where X = H) including to our mind the main types of substitutes. Salt-like compounds (of PhCOO^-M^+ and $\text{PhNR}_3^+\text{Y}^-$ type) and amide derivatives (of benzamide and N-phenylacetamide type) were excluded from the

set because their spectral data are absent in [5] or their spectra were received in the solvent differing from CDCl_3 .

All δ_i^{H} values of basic spectral parameters of mentioned set taken from spectra in CDCl_3 [5], CAP values as well as $\Delta\delta_i^{\text{H}}$ and ΔCAP differential values are represented in Table 1. CAP values are calculated by formula: $\text{CAP} = 0,2(2\delta_o^{\text{H}} + 2\delta_m^{\text{H}} + \delta_p^{\text{H}})$. Differential parameters $\Delta\delta_i^{\text{H}}$ and ΔCAP are the differences between corresponding values for substituted $\text{C}_6\text{H}_5\text{X}$ and benzene (where $\text{X} = \text{H}$ and $\Delta\delta_i^{\text{H}} = \Delta\text{CAP} = 0$). They are calculated by formula: $\Delta\delta_i^{\text{H}} = \delta_i^{\text{x}} - 7,33$ ($\Delta\text{CAP} = \text{CAP}^{\text{x}} - 7,33$). Symbols δ_i^{x} and CAP^{x} indicate parameters of substituted compounds $\text{C}_6\text{H}_5\text{X}$. Value δ_i for benzene is equal to 7,33 ppm.

Table 1.

Data of basic (δ_i^{H}), differential ($\Delta\delta_i^{\text{H}}$) and calculated average (CAP, ΔCAP) spectral parameters of 26 monosubstituted benzenes $\text{C}_6\text{H}_5\text{X}$

N	Substituent X	δ_i^{H} (CAP), ppm				$\Delta\delta_i^{\text{H}}$ (ΔCAP), ppm			
		δ_o^{H}	δ_m^{H}	δ_p^{H}	PYII	$\Delta\delta_o^{\text{H}}$	$\Delta\delta_m^{\text{H}}$	$\Delta\delta_p^{\text{H}}$	ΔPYII
1	NMe ₂	6,725	7,23	6,71	6,92	-0,60	-0,10	-0,62	-0,41
2	NH ₂	6,625	7,13	6,73	6,85	-0,70	-0,20	-0,60	-0,48
3	OH	6,82	7,22	6,92	7,00	-0,51	-0,11	-0,41	-0,33
4	OMe	6,885	7,27	6,93	7,05	-0,44	-0,06	-0,40	-0,28
5	OPh	6,995	7,30	7,07	7,13	-0,33	-0,03	-0,26	-0,20
6	SMe	7,25	7,25	7,11	7,22	-0,08	-0,08	-0,22	-0,11
7	Me	7,15	7,23	7,14	7,18	-0,18	-0,10	-0,19	-0,15
8	Et	7,18	7,26	7,15	7,21	-0,15	-0,07	-0,18	-0,12
9	i-Pr	7,215	7,27	7,15	7,22	-0,11	-0,06	-0,18	-0,11
10	t-Bu	7,385	7,29	7,16	7,30	0,06	-0,04	-0,17	-0,03
11	Ph	7,57	7,40	7,31	7,45	0,24	0,07	-0,02	0,12
12	H	7,33	7,33	7,33	7,33	0	0	0	0
13	SiMe ₃	7,52	7,33	7,33	7,41	0,19	0	0	0,08
14	F	7,03	7,31	7,10	7,15	-0,30	-0,02	-0,23	-0,18
15	Cl	7,32	7,26	7,21	7,27	-0,01	-0,07	-0,12	-0,06
16	Br	7,48	7,20	7,26	7,32	0,15	-0,13	-0,07	-0,01
17	I	7,68	7,07	7,30	7,36	0,35	-0,26	-0,03	0,03
18	CO ₂ H	8,125	7,46	7,60	7,75	0,80	0,13	0,27	0,42
19	CO ₂ Me	8,035	7,42	7,53	7,69	0,71	0,09	0,20	0,36
20	CO ₂ Et	8,045	7,42	7,53	7,69	0,72	0,09	0,20	0,36
21	CF ₃	7,61	7,46	7,53	7,53	0,28	0,13	0,20	0,20
22	Ac	7,95	7,44	7,55	7,67	0,62	0,11	0,22	0,34
23	CH=O	7,87	7,52	7,62	7,68	0,54	0,19	0,29	0,35
24	CN	7,65	7,47	7,61	7,57	0,32	0,14	0,28	0,24

25	SO ₂ Me	7,95	7,58	7,67	7,75	0,62	0,25	0,34	0,42
26	NO ₂	8,22	7,56	7,71	7,85	0,89	0,23	0,38	0,52

Substituent constants

Selection principles for Hammett constants (σ_p and σ_m) are considered at first, then – for Brown constants (σ_p^+ and σ_m^+) and then – for other types of X substituent constants.

Hammett constants (σ_p and σ_m) of substituents X

It is well-known that there are several types of X substituent constants. At the beginning of our investigations it was not clear which one may have linear dependence of δ_i^H - σ relation (if it exists at all). That is why now, during investigations of these dependencies, we decided to examine the most important (in our opinion) new and re-examine previous [3] (both Hammett and Brown) types of substitute constants using improved set of spectral parameters represented in Table 1.

It should be noted that from the fifties of last century till now for Hammett constants different literature sources often present different σ values for the same substituent X. This fact issues the challenge of “true” values selection. The decision may be in parallel usage of several selected sets of Hammett constants with following comparison of correlation results.

Earlier [3] we used only one set of Hammett constants σ_p (for the substituent located in para-position in relation to the reaction centre). Values of these constants as well as Brown constants σ_p^+ were taken from the reference-book [7]. Sets of Hammett constants (σ_m and σ_p) for 75 substituents X presented in [7] were taken in their turn by the authors from different reviews [8]. We consider that this information is still topical now; therefore Table 2 contains σ_m and σ_p values taken from [7] for all 26 types of selected substituents X.

The second used set of σ_m and σ_p constants contains data for 23 substituents represented in the work [9]. Also in Table 2 there are two “modern” sets of σ_m and σ_p constants taken from internet-sites [10, 11]. Obviously that σ_m and σ_p values given in mentioned sources seem to be the most reliable for present authors.

Given in Table 2 σ_m and σ_p values require some comments to our mind.

Constants σ_p for aniline derivatives (X = NMe₂ and NH₂) given in [7, 9, 10] are coincide with each other but differ from data [11]. The same situation is for σ_p constants of alkylbenzenes and diphenyl (X = Ph). Data from all four sources for phenol (X = OH and OMe) derivatives and chlorobenzene as well as for all electron-acceptor substituents coincide well. The σ_p constants for other haloidbenzenes are apart. For iodobenzene “new” constants are greater by

0.1 than “old” ones (0.28 from [10, 11] against 0.18 from [7, 9])¹. For fluorobenzene and bromobenzene coincident data from [7, 9, 10] differ from data given in [11]. The low value of benzaldehyde σ_p constants should be noted, especially in comparison with acetophenone constant.²

Table 2.

Values of Hammett's constants σ_M and σ_p of monosubstituted benzenes C_6H_5X , taken from [7, 9–11]

N	Substituent X	Values of constants σ_p , taken from				Values of constants σ_m , taken from			
		[7]	[9]	[10]	[11]	[7]	[9]	[10]	[11]
1	NMe ₂	-0,83	-0,83	-0,83	-0,63	-0,05	-0,21	-0,21	-0,1
2	NH ₂	-0,66	-0,66	-0,66	-0,57	-0,16	-0,16	-0,16	-0,09
3	OH	-0,37	-0,37	—	-0,38	0,121	0,12	—	0,13
4	OMe	-0,268	-0,27	-0,27	-0,28	0,115	0,12	0,12	0,1
5	OPh	-0,32	-0,32	—	—	0,252	0,25	—	—
6	SMe	0	0	—	—	0,15	0,15	—	—
7	Me	-0,17	-0,17	-0,17	-0,14	-0,069	-0,07	-0,07	-0,06
8	Et	-0,151	-0,15	-0,15	—	-0,07	-0,07	-0,07	—
9	i-Pr	-0,197	—	-0,15	—	-0,1	—	-0,07	—
10	t-Bu	-0,197	—	-0,2	-0,15	-0,1	—	-0,1	-0,09
11	Ph	-0,01	-0,01	-0,01	0,05	0,06	0,06	0,06	0,05
12	H	0	0	0	0	0	0	0	0
13	SiMe ₃	-0,07	—	—	—	-0,04	—	—	—
14	F	0,062	0,06	0,06	0,15	0,337	0,34	0,34	0,34
15	Cl	0,227	0,23	0,23	0,24	0,373	0,37	0,37	0,37
16	Br	0,232	0,23	0,23	0,26	0,391	0,39	0,39	0,37
17	I	0,18	0,18	0,28	0,28	0,352	0,35	0,35	0,34
18	CO ₂ H	0,45	0,45	—	0,44	0,37	0,37	—	0,35
19	CO ₂ Me	0,39	0,45	0,45	0,44	0,32	0,37	0,37	0,35
20	CO ₂ Et	0,45	0,45	0,45	0,44	0,37	0,37	—	0,35
21	CF ₃	0,54	0,54	0,54	0,53	0,43	0,43	0,43	0,46
22	Ac	0,502	0,5	0,5	0,47	0,376	0,38	0,38	0,36
23	CH=O	0,22	0,22	—	—	0,36	0,35	—	—
24	CN	0,66	0,66	0,66	0,7	0,56	0,56	0,56	0,62
25	SO ₂ Me	0,68	0,72	0,72	0,73	0,56	0,6	0,6	—
26	NO ₂	0,778	0,78	0,78	0,81	0,71	0,71	0,71	0,71

¹ It is possible that it is a mistake in values of mentioned constants (as well as in other cases).

² Following conclusions may be done: (i) all 4 sets of σ_p constants more or less coincide with each other; (ii) sets of coincident constants given in [7, 9, 10] essentially differ from the set given in [11].

For σ_m constants of aniline derivatives the situation is the same as for σ_p constants. The difference is that the value for dimethylaniline given in [7] is closer to the value given in [11]. For other σ_m constants: phenol derivatives, alkylbenzenes, diphenyl and electron-acceptor substituents there is a good coincidence between data from all four sources. Generally the coincidence between values of all σ_m constants is better than that of σ_p constants.

Obviously that owing to the difference between σ_m and σ_p constants from different sources and especially different number of constants in every set, we may expect essential distinctions between correlation coefficients R.

Brown's constants (σ_m^+ and σ_p^+) and other sets of constants.

Sets of σ_p^+ Brown's constants

Values of σ_p^+ Brown's constants used by us in [3] were transferred by authors [7] from the Swain's paper [12] without changes. It should be emphasized that all values of σ_p Brown's constants published in [12] are calculated values, not experimental ones. All values more or less differ from 21 experimental constants σ_p^+ given by Brown and Okamoto [13]. These experimental values were calculated from data of p-XC₆H₄C(CH₃)₂Cl hydrolysis kinetic investigations. Therefore we refused from calculated values given in [12] and used only experimental ones.

Atlas [5] represents spectra determined in CDCl₃ only for 19 monosubstituted benzenes from 21 above-mentioned compounds studied by Brown and co-workers (for two salt-like compounds PhX spectra are absent in [5]). These 19 values are represented in Table 3 as an experimental set of σ_p Brown's constants.

Besides 21 constants mentioned above, the paper [13] contains another 9 values σ_p^+ of other substituents X. These values were calculated by authors on the basis of methods differing from kinetic investigations or were determined by extrapolation from diagrams. Especially important substituents - electron-donor functional groups X = NMe₂, NH₂ and OH are among mentioned substitutes. The conclusion about the importance of such substitutes was indirectly confirmed by the fact that "modern" values of σ_p^+ constants given in [10, 11] include data for NR¹R² and OH. Moreover, these values were taken without changes from [13]. We may conclude that in [10, 11] "experimental" constants σ_p^+ and constants in brackets taken from [13] are equivalent because in both mentioned sets all values of Brown's constants σ_p^+ are given without brackets. One more important distinction should be noted. It means that σ_p^+ constant for dimethylaniline (-1.7) in [10] corresponds to the numeral in brackets given in [13]. This value (σ_p^+ constant for dimethylaniline) is equal to -1.5 in [11]. The latter numeral was one of alternative values discussed by Brown and Okamoto in [13] when choosing final variant of σ_p^+ constant for dimethylaminogroup.

In order to determine δ_i^H - σ and CAP- σ dependencies we included both sets of Brown constants σ_p^+ given in [10, 11] along with “experimental” set, as well as “combined” set of 22 constants σ_p^+ suggested by us. It consists of 19 “experimental” constants and three constants of especially important substituents: NMe₂ ($\sigma_p^+ = -1.5$), NH₂ ($\sigma_p^+ = -1.3$), OH ($\sigma_p^+ = -0.92$). Let us note that all three values were taken from [10, 11].

Thus we decided on four sets of σ_p^+ Brown's constants. They are in good agreement because all σ_p^+ values (except $\sigma_p^+ = -1.5$) are taken from the same source – Brown and Okamoto paper [13]. So we may assume satisfactory coincidence of investigation results concerning δ_i^H - σ_p^+ and CAP- σ_p^+ dependencies. Assumed difference in R values may be caused by different number of substituents in all four sets, as well as by different substituent ratio inside every set. For instance, in the set taken from [10] there are 16 Brown's constants and two of them (i.e. ~ 13 %) are for alkylbenzenes. At the same time in the set taken from [11] there are only 13 constants and four from them (i.e. ~ 30 %) are for alkylbenzenes. Moreover, data for electron-acceptor substituents are absolutely absent in this set.

Internet-site [10] represents the set of σ_m^+ Brown's constants for meta-position of substituents X but with some exceptions, inclusions and changes compared with original data from the work [13]. Data concerning σ_m^+ Brown's constants are absent in internet-site [11]. Therefore in the present paper we use both sets of σ_m^+ Brown's constants which are given in Table 3: (i) the set for 19 substituents (without constants of salt-like compounds) taken from [13] and (ii) the set for 16 substituents taken from [10].

Table 3.

Values of Brown's constants (σ_p^+ and σ_m^+) for substituents X of monosubstituted benzenes C₆H₅X

N	Substituent X	Values of Brown's constants (σ_p^+), taken from				Values of Brown's constants (σ_m^+), taken from	
		[13], «exp.»	«comb.»	[10]	[11]	[13], «exp.»	[10]
1	NMe ₂	—	-1,5	-1,7	-1,5	—	
2	NH ₂	—	-1,3	-1,3	-1,3	—	-0,16
3	OH	—	-0,92	-0,92	-0,92	—	0,05
4	OMe	-0,778	-0,778	-0,78	-0,78	0,047	—
5	OPh	—	—	—	—	—	—
6	SMe	-0,604	-0,604	—	—	0,158	—
7	Me	-0,311	-0,311	-0,31	-0,31	-0,066	-0,1
8	Et	-0,295	-0,295	—	-0,30	-0,064	—

9	i-Pr	-0,280	-0,280	—	-0,28	-0,060	—
10	t-Bu	-0,256	-0,256	-0,26	-0,26	-0,059	-0,06
11	Ph	-0,179	-0,179	-0,18	-0,18	0,109	0
12	H	0	0	0	0	0	0
13	SiMe ₃	0,021	0,021	—	—	0,011	—
14	F	-0,073	-0,073	-0,07	-0,07	0,352	0,35
15	Cl	0,114	0,114	0,11	0,11	0,390	0,40
16	Br	0,150	0,150	0,15	0,15	0,405	0,41
17	I	0,135	0,135	0,14	0,14	0,350	0,36
18	CO ₂ H	0,421	0,421	0,42	—	0,332	0,32
19	CO ₂ Me	0,489	0,489	0,48	—	0,368	0,37
20	CO ₂ Et	0,482	0,482	0,48	—	0,366	0,37
21	CF ₃	0,612	0,612	—	—	0,520	0,57
22	Ac	—	—	—	—	—	—
23	CH=O	—	—	—	—	—	—
24	CN	0,659	0,659	0,66	—	0,562	0,56
25	SO ₂ Me	—	—	—	—	—	—
26	NO ₂	0,790	0,790	0,79	—	0,674	0,73

Other types of substituent X constants

We also investigated the possibility for using other types of substituents X constants. The appearance of such sets is a result of attempts to divide substituent effect into the inductive and resonance components.

In Table 4 there are: (i) the set of σ_p^- constants given in [10]; (ii) two sets of inductive (σ_I) and resonance (σ_R^+) constants taken from [10, 11]; (iii) sets of σ^0 and $\Delta\sigma_R^+$ constants related by the expression $\sigma_R^+ = \sigma^0 + \Delta\sigma_R^+$ and taken from works by Yukawa and co-workers [14, 15]; (iv) the set of 22 “resonance constants $\sigma_R^+ = \sigma^+ + \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$ ” given in [16].

Table 4.

Values of other main types of substituents X constants of monosubstituted benzenes C₆H₅X

N	Substituent X	Values of constants σ_p^- from [10]	Values of inductive constants (σ_I) from		Values of resonance constants σ_R^+ from		Sets of Yukawa-Tsuno constants		Values of constants σ_R^+ or σ_R^- , taken from [16]
			[10]	[11]	[10]	[11]	σ^0	$\Delta\sigma_R^+$	
1	NMe ₂	—	0,06	0,06	-0,55	-0,94	-0,48	-1,30	-1,43
2	NH ₂	—	0,12	0,12	-0,50	-0,78	-0,36	-1,00	-1,23
3	OH	—	0,27	—	-0,44	—	-0,16	-0,82	-0,79
4	OMe	—	0,27	0,27	-0,42	-0,63	-0,10	-0,678	-0,71

5	OPh	—	—	—	—	—	0,07	—	-0,68
6	SMe	—	—	—	—	—	0,083	0,68	-0,71
7	Me	—	-0,05	-0,04	-0,13	-0,07	-0,124	-0,187	-0,22
8	Et	—	—	—	—	-0,07	-0,131	-0,164	-0,19
9	i-Pr	—	—	—	—	-0,08	-0,156	-0,124	-0,15
10	t-Bu	—	-0,07	—	-0,17	-0,09	-0,174	-0,082	-0,12
11	Ph	—	0,10	0,10	-0,10	-0,10	0,039	-0,218	-0,26
12	H	0	0	0	0	0	0	0	0
13	SiMe ₃	—	—	—	—	—	—	—	—
14	F	—	0,50	0,50	-0,31	-0,59	0,212	-0,285	-0,26
15	Cl	—	0,46	0,46	-0,18	-0,35	0,281	-0,167	-0,19
16	Br	—	0,44	0,44	-0,16	-0,34	0,296	-0,15	-0,16
17	I	—	0,39	0,39	-0,12	-0,23	0,298	—	-0,18
18	CO ₂ H	0,73	—	—	—	—	—	—	—
19	CO ₂ Me	0,68	—	0,30	—	0,03	—	—	0,28
20	CO ₂ Et	0,68	0,20*	—	0,16	—	—	—	—
21	CF ₃	—	0,42	0,45	0,08	0	—	—	—
22	Ac	0,87	0,20	0,28	0,16	0,05	0,502	—	0,32
23	CH=O	—	—	—	—	—	—	—	0,55
24	CN	1,00	0,56	0,56	0,08	0	0,653	—	0,29
25	SO ₂ Me	—	0,60	0,59	0,12	0	0,749	—	0,32
26	NO ₂	1,27	0,65	0,65	0,15	0	0,808	—	0,45

Thus in Tables 2-4 there are sets of 10 main (in our opinion) types of substituent X constants in monosubstituted benzenes: σ_m and σ_p Hammett constants, σ_m^+ and σ_p^+ Brown constants, σ_p^- , σ_I inductive constants, σ_p^+ resonance constants, σ^0 and $\Delta\sigma_R^+$ Yukawa-Tsuno constants, as well as resonance constants $\sigma_R^+ = \sigma^+ + \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$. The number of plots on diagrams (i.e. substituents X including hydrogen atom) in every set varies from 7 to 26 what is usual for the correlation of such type.

Results and Discussion

On the basis of above-mentioned $\Delta\delta_i^H$ and σ values using the regression equation $Y = A + BX$ and computer program Origin 5.0 the dependencies of every four differential spectral parameters ($\Delta\delta_o^H$, $\Delta\delta_m^H$, $\Delta\delta_p^H$ and ΔCAP taken from Table 1) upon all substituent X constants taken from Tables 2-4 were determined. All coefficients R calculated with the accuracy of 0.001 are represented in Table 5.

Dependencies of parameters $\Delta\delta_o^H$, $\Delta\delta_m^H$, $\Delta\delta_p^H$ and ΔCAP for benzene and its 21 monosubstituted compounds on «combined» sets of σ^+ Braun constants are described in Figs. 1, 3, 5 and 7 in accompanied paper as an examples.

Depending upon correlation coefficient R we suggest the following gradation of “linearity degree” of dependencies $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$ given in Table 5. Intervals with the same estimation of R values are determined arbitrarily and differ by values. Gradually intervals restrict at $R\rightarrow 1$. Boundaries of mentioned intervals are accepted using “round numbers” in denary system. The qualitative estimation of every interval is marked by definite amount of “+” and “-“ symbols. To our mind the suggested estimation of plots “linearity degree” on diagram is in more or less agreement with the similar common qualitative estimations of analogous values.

Coefficient R value	Qualitative estimation of plots “linearity degree” on diagram	Interval marking
0,001–0,8	“linearity” is practically absent	“_ _ _“
0,801–0,9	“linearity” exists but very bad	“_ _“
0,901–0,95	bad “linearity”	“_“
0,95–0,975	satisfactory “linearity”	“-+” till 0,965 and “+-“ for above 0,965
0,975–0,99	well “linearity”	“+”
0,99–0,995	very well “linearity”	“++”
0,995–1,0	excellent “linearity”	“+++”

From Table 5 we may conclude following:

1. A relatively small spread in values of R coefficients is obtained using sets of Hammett (σ_p) and Brown (σ_p^+) para-constants. Thus, for the four sets of σ_p Hammett constants all R values for $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$ dependencies are in the narrow intervals 0,025–0,03.

The same narrow intervals are on diagrams for dependencies $\Delta\delta_o^H-\sigma_p^+$, $\Delta\delta_p^H-\sigma_p^+$ and $\Delta\text{CAP}-\sigma_p^+$ when all four sets of Brown para-constants (σ_p^+) were used. The only one exclusion is $\Delta\delta_m^H-\sigma_p^+$ dependency. The interval of spread in values R is more wider using Hammett (σ_m) and Brown (σ_m^+) meta-constants as well as inductive and resonance constants. The reason is the nature of constants as itself and sets composition, i.e. quantitative ratio between substituent constants.

2. Actually for all 22 investigated sets of substituent X constants there is more or less clear regularity mentioned already [1-3]: the least R values are determined for dependencies $\Delta\delta_m^H-\sigma$, i.e. “linearity” for meta-protons is the worst among all spectral parameters $\Delta\delta_i^H$ and CAP. The calculated average R value is 0,64 for all 22 dependencies $\Delta\delta_m^H-\sigma$, i.e. linearity is practically absent. On the other hand the best calculated average value ($R = 0,86$) is for para-protons. For two other spectral parameters (δ_o^H and CAP) calculated average

values R for all 22 diagrams are located between mentioned values ($R = 0,81$ for CAP and $R = 0,78$ for ortho-protons).

Twenty (from 22 possible) sets of substituent constants have the same regularities as for average values R. The exclusions are sets σ_m^+ from [13] and σ_p^- . In these sets value R for meta-protons by unknown reason is anomalously high, especially in the first case (σ_m^+ from [13]) when it exceeds value R for other three spectral parameters.

3. Correlation (mark “---“) is practically absent for all sets of σ_m constants which are in meta-positions relatively to the reaction centre in phenyl ring of substituent, i.e. Hammett (σ_m) and Brown (σ_m^+) constants. In the diagrams for all these sets value R does not reach the estimation “vary bad linearity” ($R \leq 0,8$). Correlations using σ_I inductive constants are still worse. This value does not reach even 0,6.

4. On the contrary, for para-constants: σ_p Hammett constants, σ_p^+ Brown constants, σ^0 and $\Delta\sigma_R^+$ Yukawa-Tsuno constants, σ_p^- and σ_p^+ resonance constants, as well as resonance constants $\sigma_R^+ = \sigma^+ + \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$ in the diagrams of $\Delta\delta_p^H - \sigma$ (for para-protons) there is “satisfactory” estimation of linearity degree ($R \rightarrow 0,96-0,97$). The linearity is worse for CAP and ortho-protons (R is varied from 0,7 to 0,96) and the worst value is for meta-protons except for dependency on σ_p^- .

Table 5.

Correlation coefficients R values of dependencies $\Delta\delta_i^H$ - σ and Δ CAP- σ and qualitative estimation of «linearity degree» for different types of substituent constants

Parameter's type $\Delta\delta_i^H$ (Δ CAP)	Hammett's constants σ_p from				Hammett's constants σ_m from				Brown's constants σ_p^+			
	[7]	[9]	[10]	[11]	[7]	[9]	[10]	[11]	«exp.»	«comb.»	from [10]	from [11]
Quantity of substituents	26	23	19	19	26	23	18	19	19	22	16	13
$\Delta\delta_o^H$	0,885 (--)	0,899 (--)	0,893 (--)	0,901 (-)	0,685 (---)	0,758 (---)	0,691 (---)	0,772 (---)	0,829 (--)	0,888 (--)	0,886 (--)	0,862 (--)
$\Delta\delta_m^H$	0,729 (---)	0,731 (---)	0,737 (---)	0,707 (---)	0,619 (---)	0,645 (---)	0,577 (---)	0,625 (---)	0,639 (---)	0,679 (---)	0,615 (---)	0,177 (---)
$\Delta\delta_p^H$	0,939 (-)	0,947 (-)	0,959 (-+)	0,963 (-+)	0,732 (---)	0,805 (--)	0,767 (---)	0,815 (--)	0,939 (-)	0,966 (+-)	0,958 (-+)	0,952 (-+)
Δ CAP	0,907 (-)	0,918 (-)	0,921 (-)	0,924 (-)	0,711 (---)	0,779 (---)	0,721 (---)	0,792 (---)	0,870 (--)	0,913 (-)	0,901 (-)	0,884 (--)

Continuation of table 5.

Parameter's type $\Delta\delta_i^H$ (ΔCAP)	Brown's constants σ^+ _M from		Constants σ^- _p from [10]	Inductive constants σ_I from		Resonance constants σ^+ _R from		Yukawa-Tsuno constants		«resonance constants» σ^+ _R = σ^+ - σ^0 and σ^- _R = σ^- - σ^0
	[13]	[10]		[10]	[11]	[10]	[11]	σ^0	$\Delta\sigma^+$ _R	
Quantity of substituents	19	16	7	20	16	18	19	20	14	22
$\Delta\delta_o^H$	0,616 (---)	0,653 (---)	0,698 (---)	0,453 (---)	0,546 (---)	0,939 (-)	0,784 (---)	0,864 (--)	0,826 (--)	0,893 (--)
$\Delta\delta_m^H$	0,477 (---)	0,542 (---)	0,956 (-+)	0,430 (---)	0,472 (---)	0,740 (---)	0,575 (---)	0,699 (---)	0,521 (---)	0,713 (---)
$\Delta\delta_p^H$	0,694 (---)	0,741 (---)	0,972 (+-)	0,511 (---)	0,592 (---)	0,974 (+-)	0,842 (--)	0,908 (-)	0,923 (-)	0,951 (-+)
$\Delta\rho_{YII}$	0,641 (---)	0,682 (---)	0,825 (--)	0,481 (---)	0,570 (---)	0,958 (-+)	0,799 (---)	0,888 (--)	0,853 (--)	0,913 (-)

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