

II. Analysis of possible reasons of R correlation coefficients decrease in the diagrams: basic spectral parameters δ_i^H in NMR 1H spectra of monosubstituted benzenes dependencies upon substituent X constants σ ♦

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Abstract

Elimination of 4 haloidbenzenes, benzoic acid and diphenyl spectral parameters from all investigated dependencies $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$ seems to be logically grounded. Such elimination is explained by specific behavior of this compounds in NMR 1H spectra. In this connection R correlation coefficient essentially increases in all diagrams with above constants elimination.

Key words: NMR 1H spectra of monosubstituted benzenes, basic (δ_i^H) spectral parameters, sets of constants (σ), $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$ dependencies, correlation coefficient R, and differential correlation coefficient ΔR , elimination of spectral parameters, substituent plots in $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$ diagrams, “linearity degree” of dependencies $\Delta\delta_i^H-\sigma$ and $\Delta\text{CAP}-\sigma$, increase of correlation coefficient.

I. Introduction

In the first part of the communication [1], the full text of which is attached here as the appendix, we describe the results of our investigation about the dependence of the monosubstituted benzenes Ph-X spectral parameters in NMR 1H spectra on the values of substituent X constants. There were studied the following compounds Ph-X where X = NMe₂ (1), NH₂ (2), OH (3), OMe (4), OPh (5), SMe (6), Me (7), Et (8), i-Pr (9), t-Bu (10), Ph (11), H (12), Si(Me)₃ (13), F (14), Cl (15), Br (16), I (17), COOH (18), COOMe (19), COOEt (20), CF₃ (21), Ac (22), CH=O (23), CN (24), SO₂Me (25), NO₂ (26). We have investigated four NMR 1H spectral parameters of each of the 26 monosubstituted benzenes: δ_o^H , δ_m^H , δ_p^H

♦ This communication is the second and last part of whole our paper named “Investigation of the dependence of diH basic parameters in NMR 1H spectra of C₆H₅X monosubstituted benzenes upon substituent X constants s”, which, in turn, is the report N 11 on topic “THE DEPENDENCE OF NMR 1H AND 13C SPECTRAL PARAMETERS OF MONOSUBSTITUTED AROMATIC COMPOUND UPON SPATIAL-STRUCTURAL PECULIARITIES OF SUBSTITUENT IN IT”.

The first part of this report was present as our transaction on ECSOC-13 last year (2009) [1] and given in this communication as appendix.

and CAP (calculated average parameter of chemical shifts). We studied the possibility of the existence the linear dependence of the $\Delta\delta_i^H$ and CAP parameters for 22 types of substituent constants as meta- and para-Hammet's and Brown's constants (σ и σ^+), Yukawa-Tsuno constants etc. There were obtained 88 (4 x 22) dependencies $\Delta\delta_i^H$ - σ ; for each of them there were computed correlations coefficients R. We discussed this $\Delta\delta_i^H$ - σ dependences and draw some conclusions.

As it was shown above in previous communication [1], the best diagrams "linearity" of $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies is observed for those substituent constants which are connected with their resonance properties. And *vice versa*, the worst correlation is connected with the constants depending upon inductive parameters of substituents. However peculiarities of X substituent nature go beyond these two properties. At least it is obvious that their spatial characteristics essentially affect the "linearity degree" of the diagrams, especially for $\Delta\delta_o^H$ - σ dependency. This influence is less for $\Delta\delta_m^H$ - σ dependency and CAP.

Also we cannot ignore the presence of special (immanent) spectral peculiarities of the substituents. In our opinion the systematic deviation of substituent plots in $\Delta\delta_i^H$ - σ and Δ CAP- σ diagrams by using all types of substituent constants testifies to this fact.

II. The Method of regular eliminations of some substituent constants.

In order to increase the correlation coefficients R we decide to propose the method of elimination some substituent X constants σ during investigated $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies. All this eliminations are logically grounded.

II.1. Regular elimination of haloid substituent constants

The comparison of all investigated $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies for four haloidbenzenes (i.e. 4 haloid atoms as substituents ($X = \text{Hal}$)) with similar diagrams built for all X substituents in part I confirms mentioned thesis.

Examples of such "dual line" comparative diagrams are given in Figs. 1, 3, 5 and 7. As a set of substituent constants we selected the "combined" [1] vast set (22 substituents) of Brown para-constants with the best correlations. More or less similar diagrams are observed for all other above mentioned sets of constants (except the set of resonance constants for Δ CAP- σ_R and $\Delta\sigma^+_R$ Yukawa-Tsuno constants for diagrams of $\Delta\delta_p^H$ - σ and Δ CAP- σ dependencies). The ratio $\Delta R < 0$ is true for mentioned cases but ΔR absolute values are minimal, i.e. ≤ 0.004 . For other almost 80 cases $\Delta R > 0$ and its maximum value is the value for metha-protons in the case of $\Delta\delta_m^H$ dependence upon the set of constants σ^+_p taken from [2] ($\Delta R = 0.520$).

The plots related to haloid substituent (marked with blue circles in Figs. 1-8). Let us compare both lines built by least-squares method in every dual line

diagrams (Figs. 1, 3, 5 and 7). In vector arrow of curvate line for four haloidbenzenes plots the direction is corresponding to the increase of haloid serial number from fluorine to iodine. The second, i.e. main line is built for all 22 compounds including four haloidbenzenes. One can see from the diagram for ortho-protons (Fig. 1) that vector line of haloidbenzenes directs up more sharply, at the angle of 45° toward the line of all substituents. This line, in its turn, directs from the low left to the upper right corner of the diagram. Vector of haloidbenzenes in diagram for metha-protons (Fig. 3) directs down and practically perpendicularly to the line of all substituents. It means that this vector directs in anti-parallel to the vector of ortho-protons. In diagrams for para-protons (Fig. 5) and CAP (Fig. 7) both lines are closer to the parallel mutual arrangement. At the same time the angles between them and the line of all substituents are even less than an angle for ortho-protons.

Such rotation of above mentioned vector for 4 haloidbenzenes in Figs. 1, 3, 5 and 7 does not take place for other types of substituents, so we have to consider this fact as an abnormal phenomenon [3]. Therefore it seems to be the grounded decision to construct the diagram of $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies for the sets consisting of 18 substituents (excluding four constants of haloid atoms). Such diagrams for the dependencies of different spectral parameters on “combined” set consisting of 18 Brown constants (i.e. without 4 haloid substituents) are represented in Figs. 2, 4, 6 and 8.

The similar diagrams, so called diagrams with elimination of haloidbenzene constants, have been drawn for 21 of 22 sets given in Tables 2-4, part I [1]. Constants for $X = \text{Hal}$ are absent in the set of σ^- constants, hence it is impossible to eliminate them. Introduced into Table 1 parameter ΔR indicates the change of R value and is equal to the difference between values after and before elimination of haloidbenzene four parameters. New values R, qualitative estimation of their “linearity” and calculated parameters ΔR are represented in Table 1.

Pair comparison of correlation coefficients given in Figs. 1→2, 3→4, 5→6 and 7→8 indicates the increase of R value for every four types of spectral parameters, i.e. $\Delta R > 0$ in even-numbered figures.

In case of para-protons, taking as an example $\Delta\delta_p^H$ - σ^+ dependency upon “combined” set of 18 σ_p^+ Brown constants, the “linearity degree” increases considerably (Fig. 6). Since value $\Delta R = 0.023$ is relatively low in this case, the qualitative estimation changes from “satisfactory level” (“+-“, $R = 0.966$) to “very well” (“++“, $R = 0.989$).

The most impressive increase of ΔR values (see table 1) takes place in the case of $\Delta\delta_m^H$ - σ dependencies for metha-protons, i.e. in the case when plots of four haloid substituents are eliminated from almost perpendicular line. The qualitative estimation of diagram linearity essentially increases and achieves even “less satisfactory degree” (“-+“, $R = 0.957$) using the set of σ_p Hammett constants from [5]. As a rule, for metha-protons ΔR values are equal to 0.2–0.3 and more values.

For other spectral parameters of ortho- and para-protons, as well as for CAP, values ΔR are considerably less than those for meta-protons. Usually they are less than 0.1; but they increase to 0.1–0.15 for Hammett and Brown meta-constants as well as for inductive constants.

Thus elimination of halobenzene spectral parameters from all investigated dependencies seems to be logically grounded. Such elimination is explained by halobenzenes specific behavior in NMR ^1H spectra. In this connection R correlation coefficient essentially increases practically in all diagrams with halobenzene constants elimination.

Table 1

Correlation coefficients R of $\Delta\delta_i^H$ - σ and CAP- σ dependencies for all possible sets of substituent constants with the elimination of 4 constants: F, Cl, Br, and I

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^+ from			
	[9]	[10]	[5]	[2]	[9]	[10]	[5]	[2]	«exp.»	«comb.»	[5]	[2]
Quantity of substituents	22	19	15	15	22	19	14	15	15	18	12	9
$\Delta\delta_o^H$	0,911 (-)	0,922 (-)	0,922 (--)	0,927 (-)	0,745 (---)	0,811 (--)	0,755 (---)	0,848 (--)	0,868 (--)	0,918 (-)	0,925 (-)	0,910 (-)
ΔR	0,026	0,023	0,029	0,026	0,060	0,053	0,064	0,076	0,039	0,030	0,039	0,048
$\Delta\delta_m^H$	0,904 (-)	0,902 (-)	0,957 (-+)	0,936 (-)	0,874 (--)	0,887 (--)	0,875 (--)	0,933 (-)	0,906 (-)	0,905 (-)	0,891 (--)	0,697 (---)
ΔR	0,175	0,171	0,220	0,229	0,255	0,242	0,298	0,308	0,267	0,226	0,276	0,520
$\Delta\delta_p^H$	0,959 (-+)	0,964 (-+)	0,981 (+)	0,984 (+)	0,792 (---)	0,857 (--)	0,824 (--)	0,886 (--)	0,979 (+)	0,989 (+)	0,986 (+)	0,983 (+)
ΔR	0,020	0,017	0,022	0,021	0,060	0,052	0,057	0,071	0,040	0,023	0,028	0,031
Δ CAP	0,938 (-)	0,945 (-)	0,957 (-+)	0,958 (-+)	0,789 (---)	0,847 (--)	0,799 (---)	0,886 (--)	0,920 (-)	0,948 (-)	0,947 (-)	0,922 (-)
ΔR	0,031	0,027	0,036	0,034	0,078	0,068	0,078	0,094	0,050	0,035	0,046	0,038

Continuation of Table 1.

Parameter's type $\Delta\delta_i^H$ (Δ CAP)	Brown's constants σ_m^+		Constants σ_p^- from [5]	Inductive constants σ_I from		Resonance constants σ_R^+ from		Yukawa-tsumo constants		"resonance constants" $\sigma_R^+ = \sigma^+ - \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$ »
	from [11]	from [5]		[5]	[2]	[5]	[2]	σ^0	$\Delta\sigma_R^+$	
Quantity of substituents	15	12		16	12	14	15	16	11	18
$\Delta\delta_o^H$	0,761 (---)	0,758 (---)		0,546 (---)	0,672 (---)	0,948 (-)	0,792 (---)	0,893 (--)	0,837 (--)	0,913 (-)
ΔR	0,145	0,105		0,093	0,126	0,009	0,008	0,029	0,011	0,020
$\Delta\delta_m^H$	0,909 (-)	0,887 (--)		0,754 (---)	0,819 (--)	0,866 (--)	0,642 (---)	0,932 (-)	0,617 (---)	0,838 (--)
ΔR	0,432	0,345		0,324	0,347	0,126	0,067	0,233	0,096	0,125
$\Delta\delta_p^H$	0,854 (--)	0,851 (--)		0,611 (---)	0,708 (---)	0,976 (+)	0,855 (--)	0,930 (-)	0,920 (-)	0,957 (-+)
ΔR	0,160	0,110		0,100	0,116	0,002	0,013	0,022	-0,003	0,006
Δ CAP	0,823 (---)	0,811 (--)		0,602 (---)	0,717 (---)	0,957 (-+)	0,795 (---)	0,922 (-)	0,850 (--)	0,924 (-)
ΔR	0,182	0,129		0,121	0,147	-0,001	-0,004	0,034	-0,003	0,011

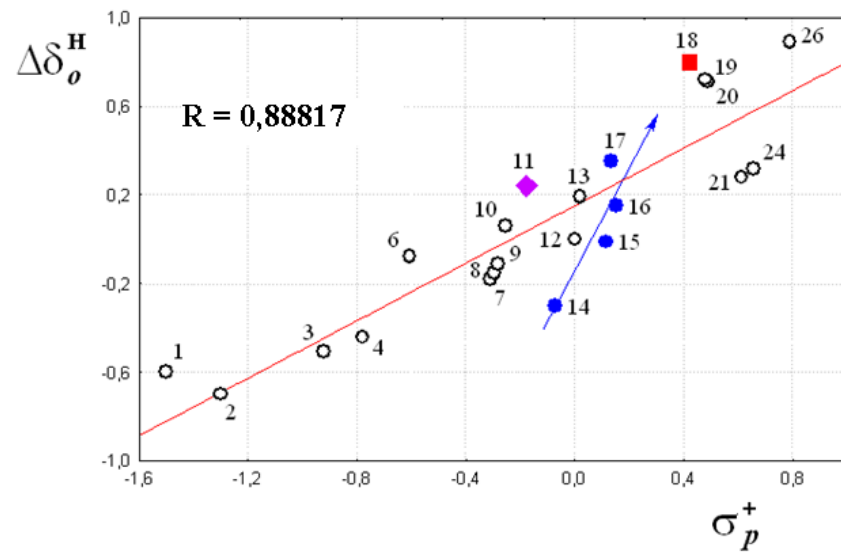


Fig. 1

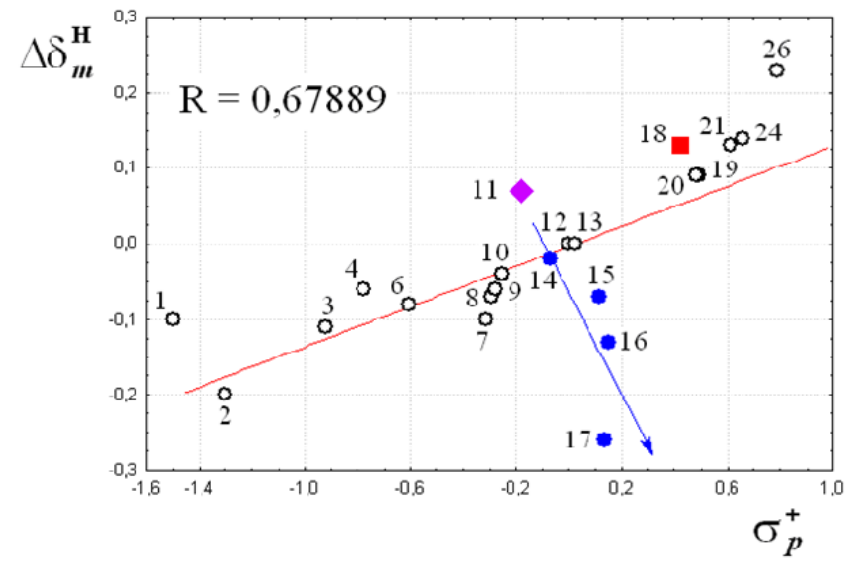


Fig. 3

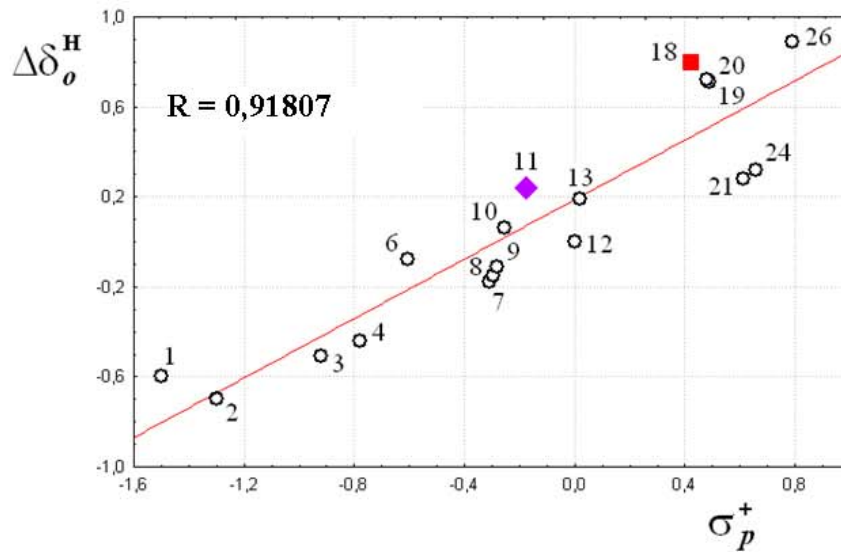


Fig. 2

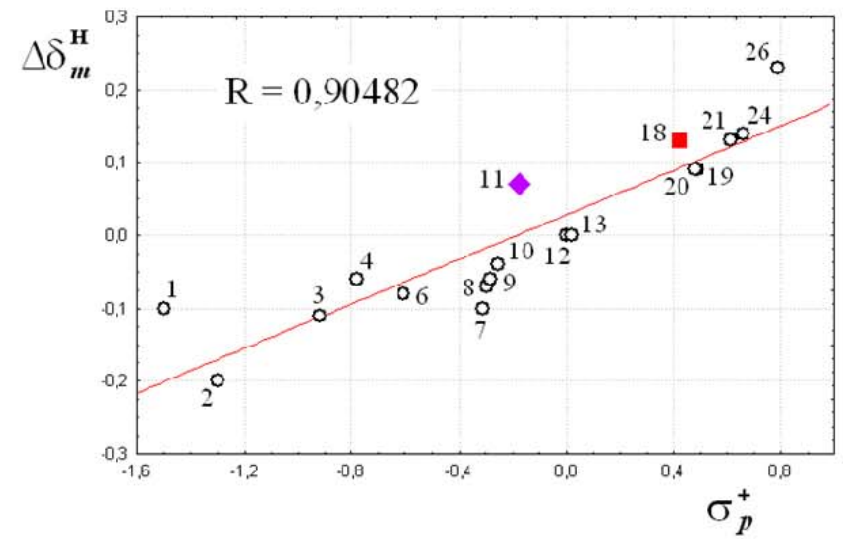


Fig. 4

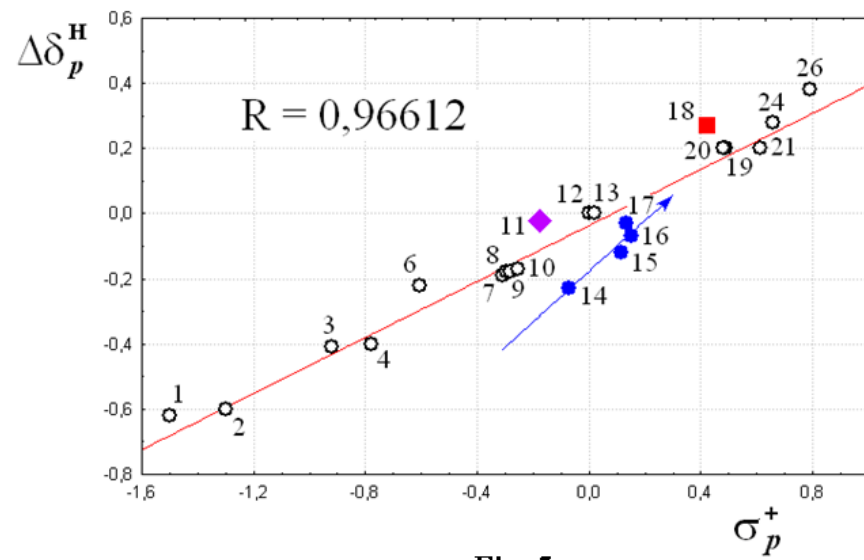


Fig. 5

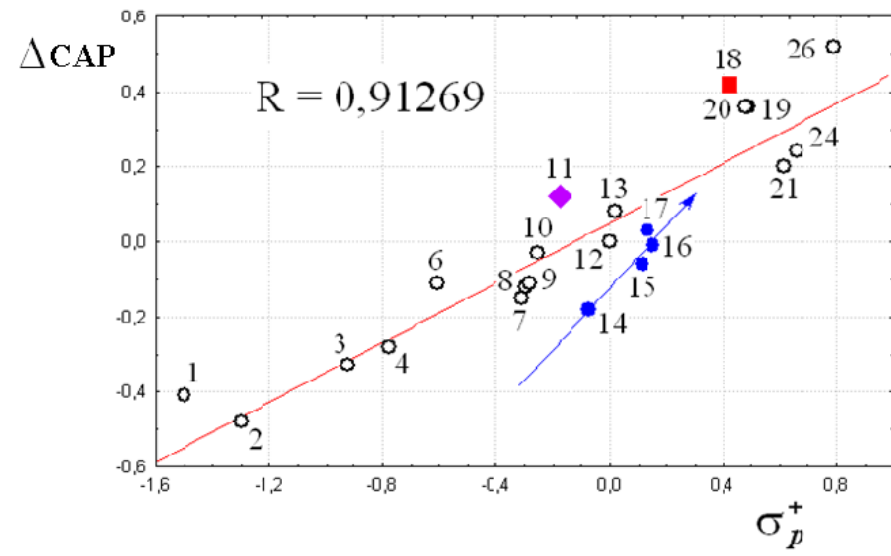


Fig. 7

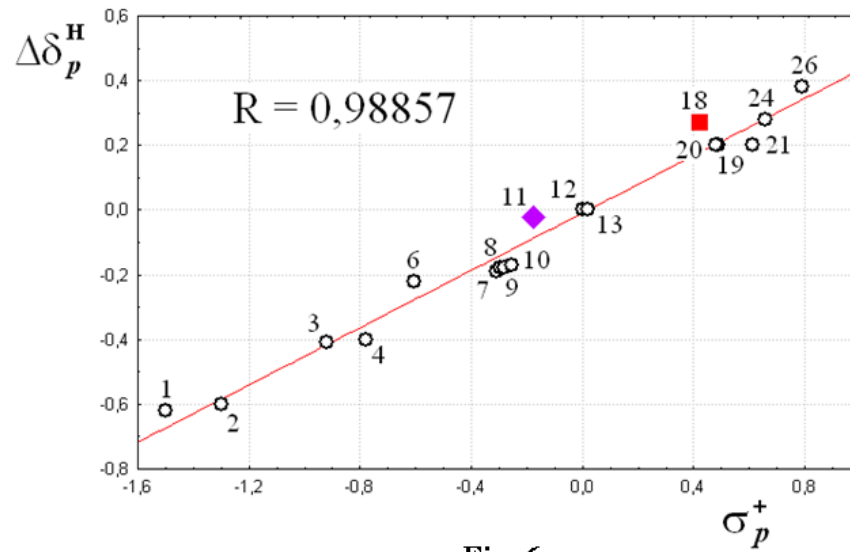


Fig. 6

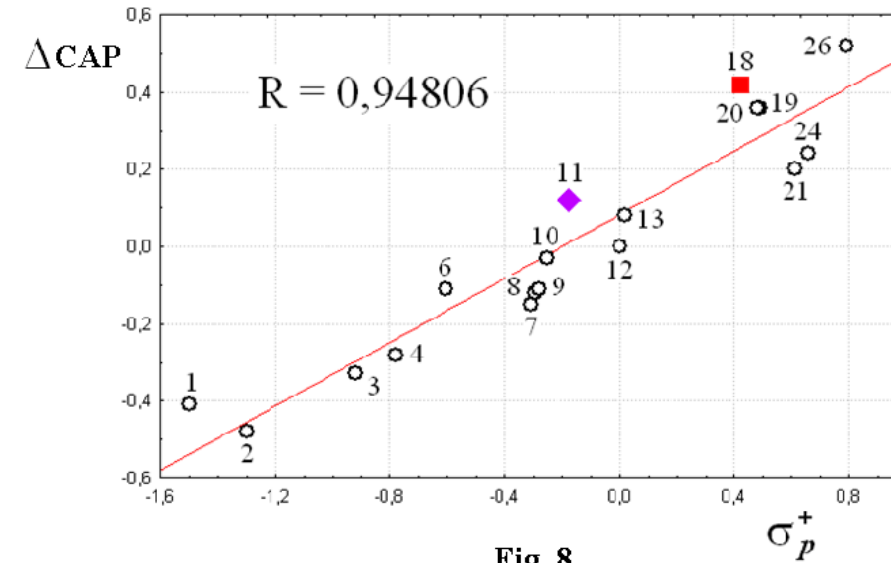


Fig. 8

II. 2. Regular elimination of other substituents X constants (X = COOH and Ph)

On account of similar reasons examined above for X = Hal, we decide to check the efficiency of regular constants elimination using carboxyl and phenyl groups as substituents X.

II. 2. 1. Carboxyl group as substituent X

The existence of abnormal spectral properties in benzoic acid justifies the decision about the possibility of carboxyl group regular elimination out of the set of substituent constants. Following arguments prove this fact. First of all, almost in all diagrams of $\Delta\delta_i^H$ - σ^+ and CAP- σ^+ dependencies the plot related to carboxyl substituent (marked with red quadrat in Figs. 1-8) is situated considerably higher than a line drawn by least-squares method. It means that all basic spectral parameters of benzoic acid (δ_o^H , δ_m^H , δ_p^H and so calculated spectral parameter - CAP) shift to the down field. At the same time all types of σ constants for COOH and COOR substituents are practically the same or they are commensurable values. Therefore, we may assume that the shift of all δ_i^H and CAP parameters to down field is an immanent spectral property of carboxyl group in benzoic acid.

The second argument is following. It is known that in NMR ^{19}F spectra of metha-substituted fluorobenzenes [6] additional shifts are appeared using formic and trifluoroacetic acids as solvents in comparison with spectral data of the same substances in other solvents. The most probable reason is acid properties of formic and trifluoroacetic acids. Since benzoic acid ($\text{pK}_a = 4.21$) is commensurable with formic acid ($\text{pK}_a = 3.75$) we may assume that downfield shift of protons absorption in NMR ^1H spectra of benzoic acid in CDCl_3 is caused by the presence of carboxyl group in it (by analogy with NMR ^{19}F spectra of substituted fluorobenzenes in acids).

II. 2. 2. Phenyl group as substituent X

The reason by which phenyl group as substituent X in diphenyl also may be attributed to the substituents recommended for elimination in order to prove correlation is an abundant effect of conjugation on spectral parameters. Moreover, as it was expected, this “superconjugation” effect is greater for para- and ortho-protons. The less effect is for CAP and the minimum one (if it appears at all) – for metha-protons. In Figs. 1-8 diphenyl plots are marked as violet rhombs.

Following diphenyl spectral parameters may be adduced as a proof. To our mind the absorption value of para-protons ($\delta_p^H = 7.31$ ppm) is too high because of “superconjugation”. The absorption value of para-protons ($\delta_p^H = 7.37$ ppm) [7] is still higher in para-terphenyl, where conjugated chain is still longer due to the inclusion of additional phenyl ring in it. The difference of 0.06 ppm appeared as a result of transfer from diphenyl to 4-terphenyl is caused in higher degree by mentioned “superconjugation” and in less degree – by increased electron-acceptor

properties of 4-biphenyl substituent in terphenyl in comparison with phenyl groups in diphenyl.

The second argument is the existence of additional chemical shift of para-protons in α -methylstyrene ($\delta_p^H = 7.24$ ppm) [6] to the upper field in comparison with above mentioned value for diphenyl (7.31 ppm). The difference between spatial demands and electron-acceptor properties of phenyl group in diphenyl on the one hand and 2-propenyl group in α -methylstyrene on the other hand must be negligible in order to change δ_p^H value. The main distinction of the this substituents affecting δ_p^H value is the elongated conjugated chain in diphenyl in comparison with triple-substituted double bond C=C in α -methylstyrene. And this factor namely maximally contributes to the observed difference of chemical shifts (-0.07 ppm).

The same as in a previous case with haloidbenzenes, we sequentially eliminate two abovementioned constants from all of 22 examined sets, presented in tables 2-4 in [1]. At first we eliminate carboxyl group constant (COOH) and then – phenyl group constant. Table 2 represents only final results of correlation coefficients change using all 22 sets (intermediate results – values R and ΔR after elimination of only carboxyl group – are the same as for the results presented in Table 2).

Parameter ΔR^I in it is also means a difference between correlation coefficients obtained with and without elimination of all 6 substituent constants. Diagrams of $\Delta\delta_i^H$ - σ and CAP- σ dependencies using “combined” set of σ^+ Brown constants [1] are represented in Figs. 9-12. This “combined” set is obtained using the set consisting of 16 constants σ^+ , i.e. at elimination of 6 substituent constants: F, Cl, Br, I, COOH and Ph.

One can see from Table 2 that the additional elimination of two substituent constants increases the “linearity” of diagrams practically in all cases, i.e. $\Delta R^I > R$ as a rule. The only one exclusion is the dependency of ΔCAP upon set of σ^+_{R} constants taken from [2].

The best result is achieved in diagrams of $\Delta\delta_p^H$ dependency on σ^+ Brown constants for all four sets. In two cases R value achieves 0.989 and closely approaches to the qualitative marking “++” and in other two cases it exceeds mentioned value. “Very well linearity” is achieved using combined set of 16 Brown constants (Fig. 11). Value R = 0.993 is the maximum one from all values represented in Tables 1,2 and Table 5 in part I [1]. Thus, diagrams “linearity” is essentially improved by regular and logically founded eliminations of the constants having “abnormal” spectral properties from corresponding sets of constants.

III. Some other interesting notes, in part related to using proposed elimination method.

Studying data of Tables 1, 2 (and Table 5 in part I [1]) some else regularities should be noted.

1. The average value of R coefficient (0.81) calculated from data of Table 5 in [1] for $\Delta\text{CAP}-\sigma$ dependency unexpectedly is founded to be too high. Although it is lower than average value R for para-protons (0.86), it is higher than average values for ortho- and metha-protons (0.78 and 0.64 correspondingly). If we calculate value R from contributions of every above mentioned average values for all three protons type we should obtain more lower value: $\frac{(0.64 \cdot 2) + (0.78 \cdot 2) + 0.86}{5} = 0.74$. The analogous relations between founded and calculated average values of R coefficients for $\Delta\text{CAP}-\sigma$ dependencies are the same for others types of σ -constants after above mentioned regular eliminations of constants out of the sets.

One of the explanations of this paradox may be a suggestion that at calculations of $\Delta\text{CAP}-\sigma$ dependencies mutual compensations of chemical shifts take place, e.g. for metha- and para-protons. As a result, the average value of R coefficient increases.

2. The increase of average values R for every four spectral parameters is calculated with the accuracy of 0.01 using 22 full sets of substituent constants (i.e. without elimination). The same 22 sets are used for the calculations with two eliminations [i) haloids; ii) (Ph + COOH)]. For the case with one elimination (4 haloids) 21 sets are used for calculations in accordance with the reasons mentioned above. For $\Delta\delta_o^H$ parameter the average values R change as follows: 0.78→0.84→0.85; for $\Delta\delta_m^H$ parameter: 0.64→0.85→0.87; for $\Delta\delta_p^H$ parameter: 0.86→0.90→0.91; for CAP – 0.81→0.87→0.89.

Let us notice that the greatest increase of average values R takes place in case with metha-protons. After two eliminations R value increases by 0.23; other three parameters increase by the range from 0.05 to 0.08. Already after first elimination (haloids) the average correlation coefficient for metha-protons exceeds R value for ortho-protons (0.85>0.84). Obviously that elimination of described above practically perpendicular vector of haloidbenzenes for dual line diagram (see Fig. 3) essentially increases R value (by 0.21) whereas for other three spectral parameters elimination of haloidbenzenes vectors close to parallel arrangement (see Figs. 1, 5 and 7) increases correlation coefficient only slightly. On the other hand, the second elimination of substituent constants (COOH + Ph) regularly increases R constants in all four cases, though by slight value (0.01–0.02). Therefore we may assume that elimination of mentioned constants is justified.

After two eliminations (i.e. six substituents) average values R for all four spectral parameters come close. This fact is evident from narrowing of interval in which they are (0.91 – 0.85 = 0.06 instead of 0.86 – 0.64 = 0.22 which was before elimination).

Table 2

Correlation coefficients R of $\Delta\delta_i^H$ - σ and CAP- σ dependencies for all possible sets of substituent constants with the elimination of 6 constants: F, Cl, Br, I, COOH and Ph

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^+ from			
	[9]	[10]	[5]	[2]	[9]	[10]	[5]	[2]	«exp.»	«comb.»	[5]	[2]
Quantity of substituents	20	17	13	14	20	17	12	14	13	16	10	8
$\Delta\delta_o^H$	0,917 (-)	0,932 (-)	0,939 (-)	0,935 (-)	0,755 (---)	0,838 (--)	0,788 (---)	0,862 (--)	0,888 (--)	0,929 (-)	0,933 (-)	0,947 (-)
ΔR	0,032	0,033	0,046	0,034	0,070	0,080	0,097	0,090	0,059	0,041	0,047	0,085
$\Delta\delta_m^H$	0,907 (-)	0,906 (-)	0,963 (+)	0,941 (-)	0,889 (--)	0,909 (-)	0,913 (-)	0,951 (+)	0,932 (-)	0,912 (-)	0,890 (--)	0,730 (---)
ΔR	0,178	0,175	0,22	0,234	0,270	0,264	0,336	0,326	0,293	0,233	0,275	0,553
$\Delta\delta_p^H$	0,960 (-+)	0,966 (+-)	0,985 (+)	0,986 (+)	0,794 (---)	0,869 (--)	0,840 (--)	0,893 (--)	0,989 (+)	0,993 (++)	0,989 (+)	0,991 (++)
ΔR	0,021	0,019	0,026	0,023	0,062	0,064	0,073	0,078	0,050	0,027	0,031	0,039
Δ CAP	0,942 (-)	0,952 (-+)	0,969 (+-)	0,965 (+-)	0,799 (---)	0,870 (--)	0,831 (--)	0,900 (-)	0,941 (-)	0,958 (-+)	0,955 (-+)	0,963 (-+)
ΔR	0,035	0,034	0,048	0,041	0,088	0,091	0,110	0,108	0,071	0,045	0,054	0,038

Continuation of table 2.

Parameter's type $\Delta\delta_i^H$ (Δ CAP)	Brown's constants σ_m^+		Constants σ_p^- from [5]	Inductive constants σ_I from		Resonance constants σ_R^+ from		Yukawa-tsunno constants		"resonance constants" $\sigma_R^+ = \sigma^+ - \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$
	from [11]	from [5]		from [5]	from [2]	from [5]	from [2]	σ^0	$\Delta\sigma_R^+$	
Quantity of substituents	13	10	6	15	11	13	14	15	10	17
$\Delta\delta_o^H$	0,785 (---)	0,808 (--)	0,741 (---)	0,566 (---)	0,705 (---)	0,950 (-+)	0,791 (---)	0,908 (-)	0,876 (--)	0,924 (-)
ΔR	0,169	0,155	0,043	0,113	0,159	0,011	0,007	0,044	0,050	0,031
$\Delta\delta_m^H$	0,935 (-)	0,887 (--)	0,964 (-+)	0,779 (---)	0,857 (--)	0,869 (--)	0,640 (---)	0,948 (-)	0,670 (---)	0,844 (--)
ΔR	0,458	0,345	0,008	0,349	0,385	0,129	0,065	0,249	0,149	0,131
$\Delta\delta_p^H$	0,863 (--)	0,880 (--)	0,992 (++)	0,621 (---)	0,726 (---)	0,976 (+)	0,856 (--)	0,937 (-)	0,935 (-)	0,958 (-+)
ΔR	0,169	0,139	0,020	0,110	0,134	0,002	0,014	0,029	0,012	0,007
Δ CAP	0,846 (--)	0,860 (--)	0,862 (--)	0,622 (---)	0,748 (---)	0,959 (-+)	0,794 (---)	0,936 (-)	0,897 (--)	0,929 (-)
ΔR	0,205	0,179	0,037	0,141	0,178	0,001	-0,005	0,048	0,044	0,016

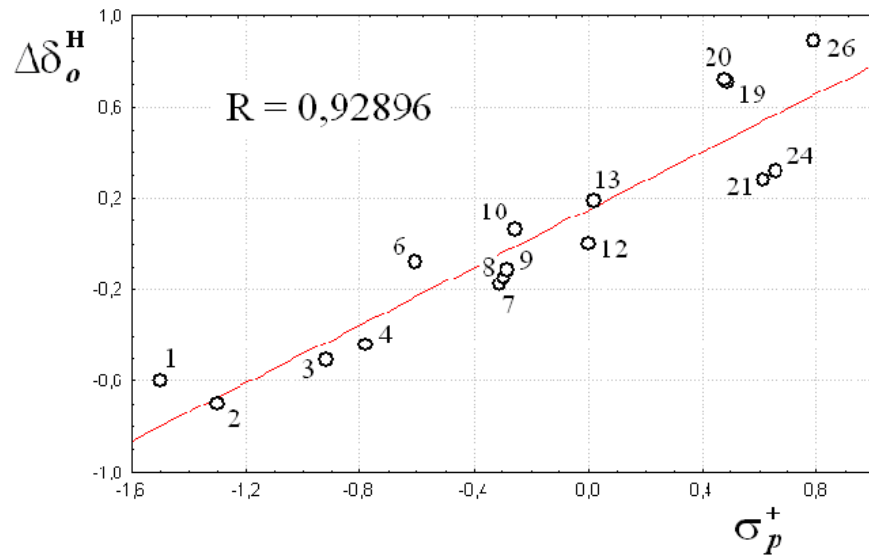


Fig. 9

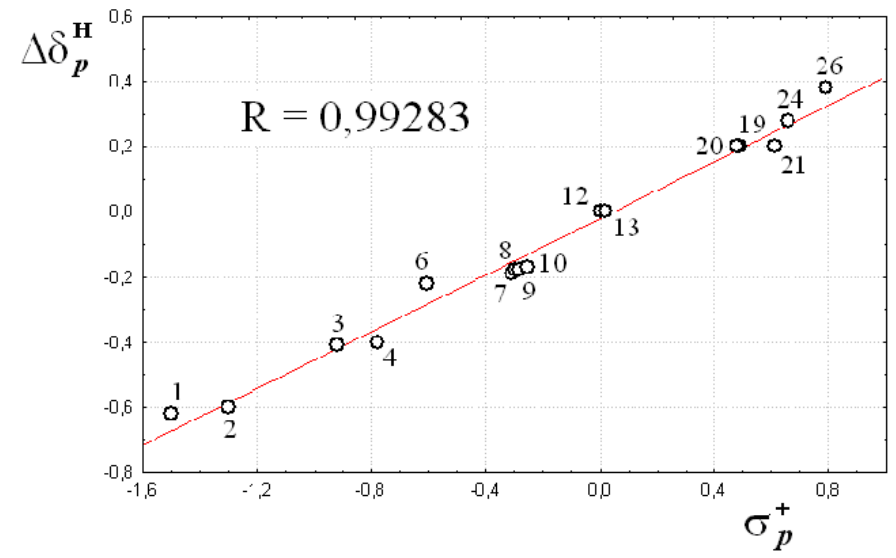


Fig. 11

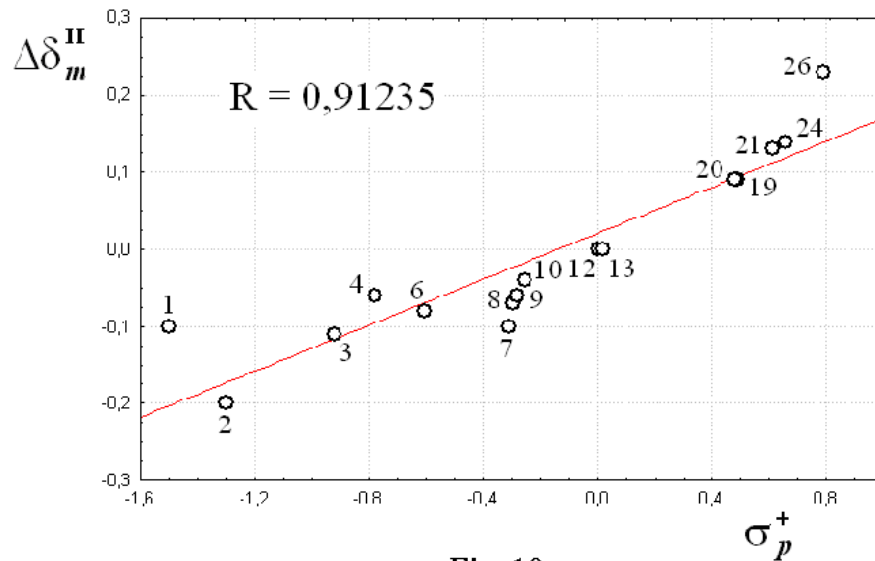


Fig. 10

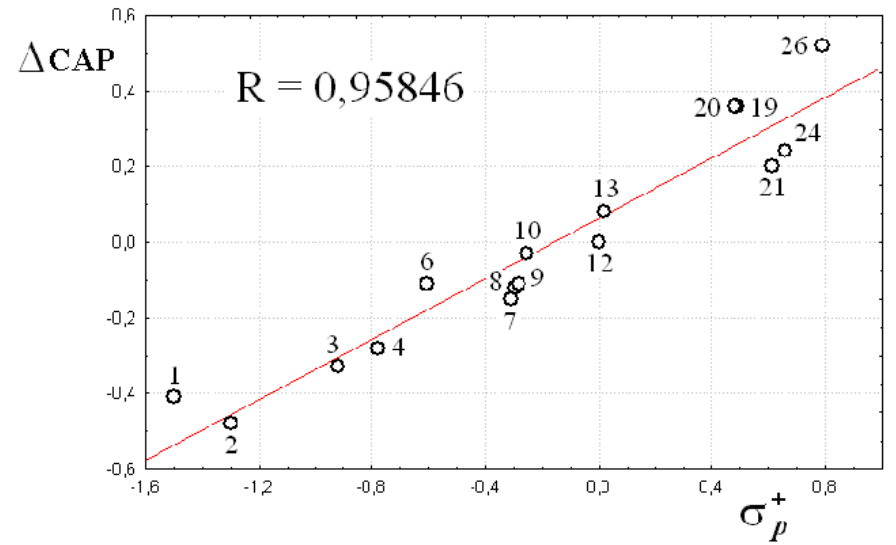


Fig. 12

3. Comparing average values R for four sets of Hammett para-constants (σ_p) with R average values obtained using four sets of Brown para-constants (σ_p^+) for every 4 differential spectral parameters ($\Delta\delta_i^H$, ΔCAP) interesting relations are observed. As it was mentioned above the best correlations for constants of both types are observed for para-protons. Let us illustrate the results of eliminations in these cases similarly to the results discussed above for the average (from 21 or 22 sets of constants) value R . Thus, for four sets of Hammett constants (σ_p) the average value R changes with accuracy of 0.001 as following: $0.952 \rightarrow 0.972 \rightarrow 0.974$. The similar change for Brown constants (σ_p^+) is: $0.954 \rightarrow 0.984 \rightarrow 0.991$. In all three cases the “linearity” of diagrams is better for the dependency of $\Delta\delta_p^H$ upon Brown constants comparing with the same dependency upon Hammett constants. Using full sets (without eliminations) in both cases the correlation is “satisfactory” (“-+”) and the difference between R values is negligible (0.954 against 0.952). The first elimination (of haloids) improves the “linearity” of $\Delta\delta_p^H$ - σ_p^+ diagram to the qualitative estimation “well” whereas for $\Delta\delta_p^H$ - σ_p diagram the “linearity” is the same (“satisfactory” level, “+-“). The second elimination of COOH and Ph constants improves correlation in greater degree to the estimation “very well” (“++”) for Brown constants and only slightly improves it for Hammett constants (the estimation remains “satisfactory” (“+-“), although it approaches to “+”).

In contrast to the case with para-protons the opposite relations of diagrams “linearity” are observed for other three spectral parameters. For $\Delta\delta_o^H$ parameter the average values R in $\Delta\delta_o^H$ - σ_p dependencies (i.e. for Hammett constants) change as follows: $0.893 \rightarrow 0.921 \rightarrow 0.931$; for $\Delta\delta_m^H$ parameter: $0.726 \rightarrow 0.925 \rightarrow 0.929$; for CAP – $0.918 \rightarrow 0.950 \rightarrow 0.957$. At the same time for $\Delta\delta_o^H$, $\Delta\delta_m^H$ and ΔCAP dependencies upon Brown constants (σ_p^+) following changes take place: $0.867 \rightarrow 0.905 \rightarrow 0.924$ for ortho-protons; $0.528 \rightarrow 0.850 \rightarrow 0.866$ for metha-protons and $0.892 \rightarrow 0.934 \rightarrow 0.954$ for CAP.

Obviously that in all cases correlation is better using Hammett constants in comparison with Brown constants. But at the same time the increase of number of eliminations for ortho-protons and CAP (the same as for para-protons) accelerates the improvement of diagram “linearity” for Brown constants compared with Hammett ones. Thus, at the elimination of six substituent constants R values become closer: 0.931 against 0.924 for ortho-protons and much more closer - 0.957 against 0.954 achieving “satisfactory linear degree” for CAP. For metha-protons, in spite of eliminations, the qualitative difference between “linear degrees” remains the same. It is improved to the estimation “very bad” (“--“) for Brown constants. But when using Hammett constants are used the value R increases to 0.929 (what is almost equal to $R = 0.931$ for ortho-protons).

4. The application of sets of Hammett (σ_m) and Brown (σ_m^+) metha-constants in all cases leads to the worse correlation compared with analogous

sets of para-constants. From other hand it should be noted that for metha-protons the maximum elimination of six substituent constants results in maximum increasing of average values R compared with those increasing, founded for other spectral parameters. At the same time this average metha-values R given in table 2 (averaged from 4 parameters for σ_m and from 2 parameters for σ_m^+) exceed value of 0.9 (0.915 for σ_m and 0.911 for σ_m^+). The same regularity is observed for both sets of inductive constants σ_I , although R values are considerably lower (~ 0.8). Relatively high value $R = 0.948$ is obtained after two eliminations and observed in $\Delta\delta_m^H$ - σ dependency using the set of σ^0 constants represented in [7]. This fact and other observations indirectly confirm the opinion that σ^0 constants should be examined together with inductive and metha-constants, but not with resonance and para-constants.

Hence, constants with the inductive properties in their basis, i.e. Hammett and Brown metha-constants, as well as Taft and Yukawa-Tsuno inductive constants, correlate better not with chemical shifts of ortho- or para-protons but with those of metha-protons. In this regard the mentioned correlation looks like dependencies of $\Delta\delta_m^F$ spectral parameters in NMR ^{19}F spectra of metha-substituted fluorobenzenes upon σ_I inductive constants except for the fact that diagrams “linearity” of $\Delta\delta_m^F$ - σ_I dependency is essentially higher ($R \gg 0.95$) [6].

5. It should be stressed that used sets of constants are unequal by quantitative and qualitative composition of the substituents. Therefore some “defective” sets are useless for in-depth analysis. Thus, for example, the set of σ^- constants presented in [5] contains only 6 electron-acceptor substituents plus hydrogen atom. It does not contain constants of electron-donor substituents and even constants of haloid substituents. Hence, the sufficiently high diagrams “linearity” of $\Delta\delta_m^H$ - σ^- and $\Delta\delta_p^H$ - σ^- dependencies is not of great value. The similar situation is for sets of σ_R resonance constants taken from both internet-sites, as well as for $\Delta\sigma_R^+$ Yukawa-Tsuno constants. In all these sets constants of electron-acceptor substituents are ignored (values of σ_R^+ are absent or equal to zero [2] or have disproportionately low positive values [5]). Diagrams of ΔCAP dependency upon the set of σ_R constants taken from [2] and [5] are represented in Figs. 13 and 14 for illustration.

6. Obviously that totality of plots crowded in the right upper corner of Fig. 13 belongs to the electron-acceptor substituents and illegitimately increases line slope to abscissa axis drawn by least-squares method. The line is steeper than it has to be, therefore plots of hydrogen and alkyl groups are situated disproportionately far below it. Due to the considerable diversity of plots in the diagram (above and below the line situated in the right part of the diagram) correlation coefficient $R = 0.799$ does not reach even the estimation “very bad correlation”. Obviously that elimination of both phenyl group and haloid substituents constants does not increase R value but, on the contrary, decreases it.

Fig. 14 represents the diagram of $\Delta\text{CAP}-\sigma_{\text{R}}$ dependency where substituent constants are taken from [5]. This diagram differs from that in Fig. 13 by the positive values of electron-acceptor groups. In our opinion these values are illegitimately low. Correlation coefficient R increases to 0.958. However, the same as in a previous case, plots of hydrogen and methyl group are situated below the least-squares line and plots of methylsulfonic and nitrous groups – above it. The same as in a previous case, elimination of haloids and phenyl group constants practically does not change R value.

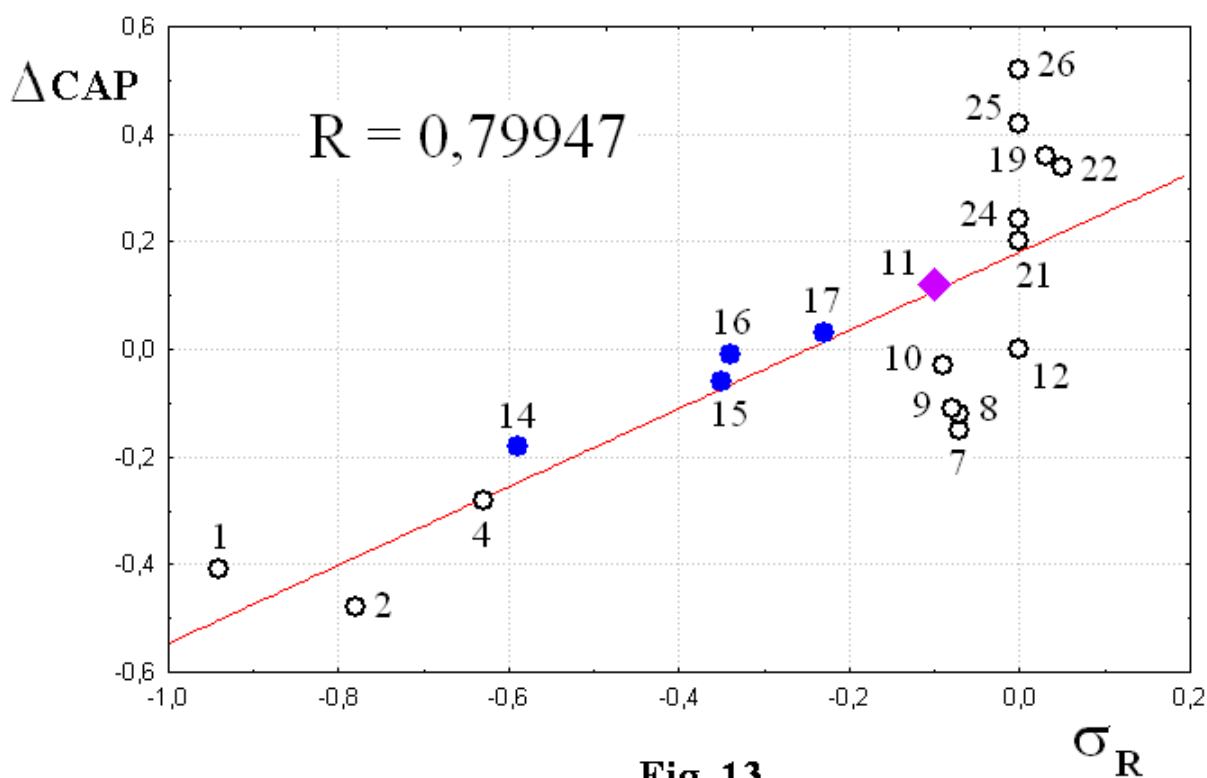


Fig. 13

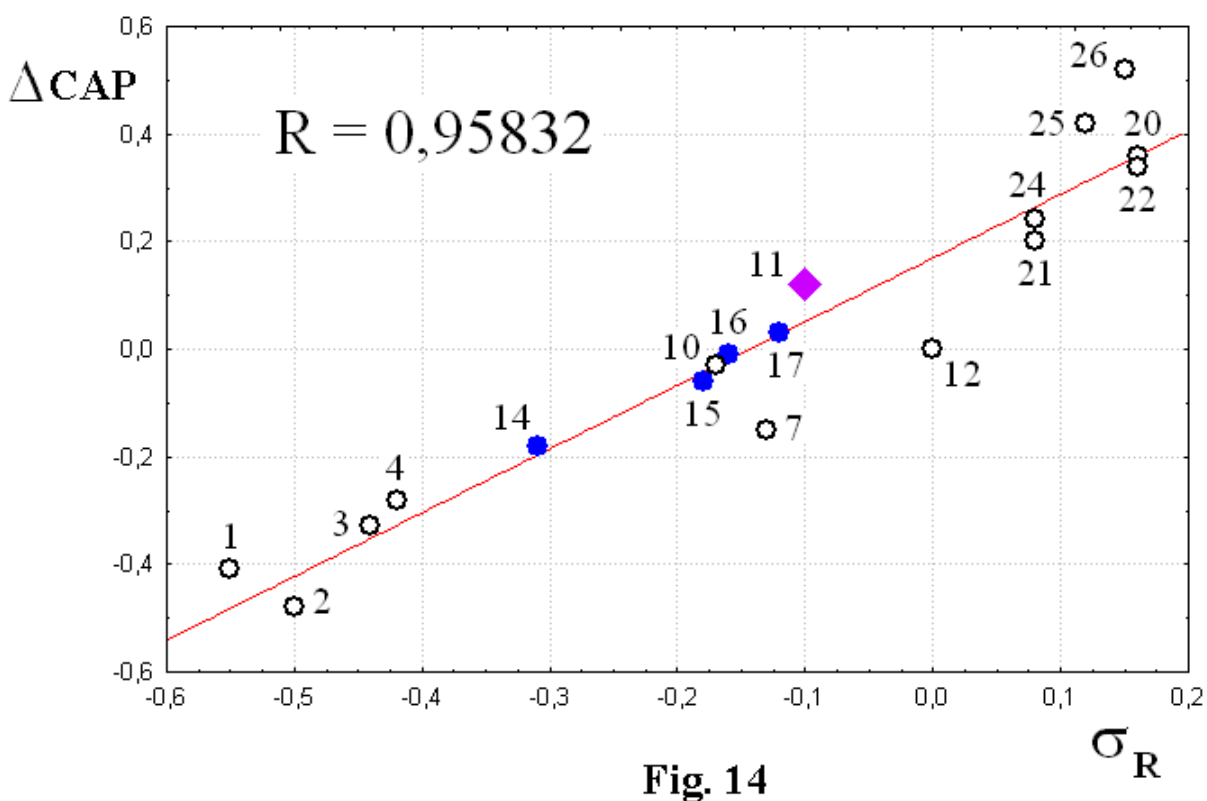


Fig. 14

7. It is interesting to note that negative values of typical electron-donor substituents – NMe_2 , NH_2 , OMe in the set of σ_R constants given in [2] are higher in 1.5 times than those given in [5] (see Table 4 in part I [1]). The greater difference (in two times or more) is observed for haloids and alkyl groups.

Moreover, this difference is opposite by absolute value in latter case. Therefore the least-squares line in Fig. 13 is more flat than the line in Fig. 14. This is the possible explanation of better correlation in latter diagram. The similar situation is typical also for diagrams of $\Delta\delta_p^H$ - σ_R dependencies which are drawn using the set of σ_R constants from [2] and [5].

There is a discrepancy between both sets of σ_R constants. In spite of the presence of approximate proportionality for the constants of electron-donor substituents including haloids, σ_R values are equal in both sets for phenyl group ($\sigma_R = -0.10$). And as regards to alkyl groups the higher absolute values for the same radicals (Me, Bu¹) are in the set taken from [5]. This fact and also great difference between the same constants of both electron-donor and electron-acceptor types of substituents casts doubt on the correctness of σ_R constants from [2] and [5]. As a result, the advisability of constant quantitative division by inductive and resonance components is also open to question [12].

8. It should be noted also that σ_R constants are negative for all four haloid atoms (in contrast to other types of substituent constants) resulting in the best proportionality to Δ CAP values. One can see from Figs. 13 and 14 that plots of every four haloidbenzenes are situated either directly on the least-squares line or directly close to it. Therefore elimination of haloid substituent constants does not increase but decreases R coefficient.

The similar situation is for $\Delta\delta_p^H$ - σ_R (in higher degree) and $\Delta\delta_o^H$ - σ_R (in less degree) dependencies but it is untypical for $\Delta\delta_m^H$ - σ_R dependency.

9. Let us examine two last non-analyzed types of substituent constants: σ^0 and “resonance constants $\sigma_R^+ = \sigma^+ - \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$ ”.

We consider that σ^0 constants are not enough suitable for the description of $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies, as well as other constants based on substituent inductive properties (σ_m and σ_m^+ metha-constants and σ_I inductive constants). The explanation is, to our mind, that all these types of constants have illegitimately low negative (even sometimes positive) values for electron-donor substituents.

The set of “resonance constants $\sigma_R^+ = \sigma^+ - \sigma^0$ and $\sigma_R^- = \sigma^- - \sigma^0$ ” is the most acceptable for mentioned purpose, especially for $\Delta\delta_p^H$ - σ dependency. However, judging from correlation coefficients R this set is worse for plotting of $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies compared with the set of Brown and Hammett para-constants.

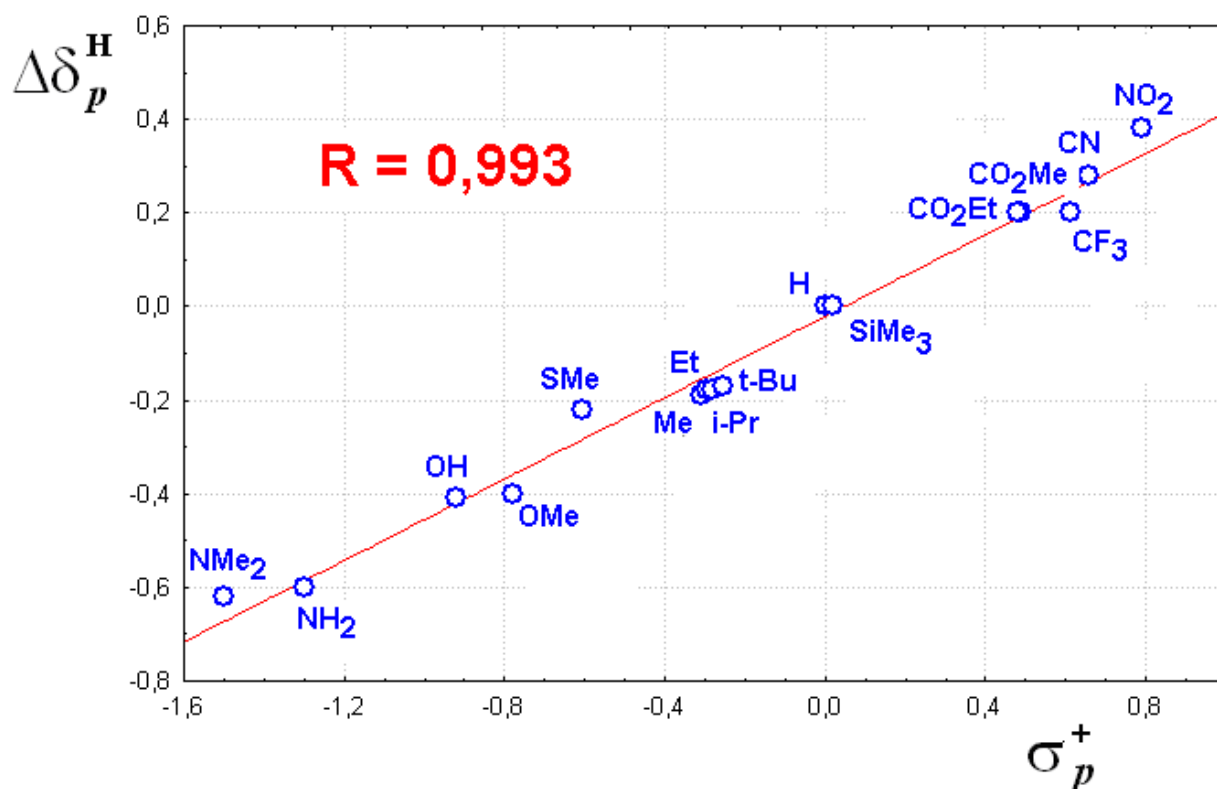
10. Illegitimately low (in our opinion) value of σ_p Hammett constant for aldehyde group (0.22) was mentioned above. If we eliminate it (in addition to constants of 6 substituents: F, Cl, Br, I, COOH and Ph) while plotting of $\Delta\delta_p^H$ - σ dependency for the set consisting of 19 constants taken from [9], then correlation coefficient increases considerably (from 0.960 to 0.974). The similar increase (0.967→0.984) takes place using the set taken from [10]. Such increase

confirms the low (and erroneous to our mind) value of σ_p Hammett constant for aldehyde group.

GENERAL CONCLUSIONS

1. So, we can conclude that linear dependency of monosubstituted benzenes NMR ^1H spectral parameters of substituent constants (σ) is really exist. The best example of this thesis is pictured at Fig. 15 which is some modifying diagram 11.

Fig.15



2. Obviously, the best linear dependencies of monosubstituted benzenes NMR ^1H spectral parameters of substituent constants (σ) are 2 dependencies, connected with $\Delta\delta_p^H$ parameter: $\Delta\delta_p^H - \sigma_p$ and $\Delta\delta_p^H - \sigma_p^+$. After all abovementioned eliminations of some substituent constants the correlation coefficients of these dependencies linearity reaches or even overcomes value 0.99.

Acknowledgements

This work was performed within the bounds of national project “Determination of the general regularities defining the values of chemical shifts

in ^1H NMR and CMR spectra depending on the chemical structure of organic substances”. Theme № В 802-2010.

We express our gratitude to National Institute of Advanced Science and Technology (SDBS Web://riodb.01.ibase.aist.go.jp/sdbs) for NMR ^1H data using in this article.

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[12] We plan to research this problem more deeply in future.

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APPENDIX.

Investigation of the dependence of δ_i^H basic spectral parameters in NMR 1H spectra of C_6H_5X monosubstituted benzenes upon substituent X constants σ

Part I.

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Abstract

The dependences of differential spectral parameters ($\Delta\delta_i^H$) in spectra NMR 1H of monosubstituted benzenes C_6H_5X 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 ($\Delta\delta_i^H$) spectral parameters, calculated average parameter of chemical shifts (CAP), substituent constants (σ), sets of constants (σ), $\Delta\delta_i^H$ - σ and Δ CAP- σ dependencies, correlation coefficient R, “linearity degree” of dependencies $\Delta\delta_i^H$ - σ and Δ CAP- σ .

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 C_6H_5X 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 δ_i^H - σ and CAP- σ 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 C_6H_5X 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 $\text{PhNR}_3^+Y^-$ 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 $\Delta\delta_i^H$ and ΔCAP differential values are represented in Table 1. CAP values are calculated by formula: $\text{CAP} = 0,2(2\delta_o^H + 2\delta_m^H + \delta_p^H)$. Differential parameters $\Delta\delta_i^H$ and ΔCAP are the differences between corresponding values for substituted $\text{C}_6\text{H}_5\text{X}$ and benzene (where X = H and $\Delta\delta_i^H = \Delta\text{CAP} = 0$). They are calculated by formula: $\Delta\delta_i^H = \delta_i^X - 7,33$ ($\Delta\text{CAP} = \text{CAP}^X - 7,33$). Symbols δ_i^X and CAP^X indicate parameters of substituted compounds $\text{C}_6\text{H}_5\text{X}$. Value δ_1 for benzene is equal to 7,33 ppm.

Table 1.

Data of basic (δ_i^H), differential ($\Delta\delta_i^H$) 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				$\Delta\delta_i^H$ (ΔCAP), ppm			
		δ_o^H	δ_m^H	δ_p^H	PYII	$\Delta\delta_o^H$	$\Delta\delta_m^H$	$\Delta\delta_p^H$	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 fluorobebzene 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 C₆H₅X, 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

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].

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

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 C_6H_5X

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 C_6H_5X

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 $\Delta CAP-\sigma$ 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 $\Delta CAP-\sigma$ 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 (-+)
$\Delta\rho_{\text{YII}}$	0,641 (---)	0,682 (---)	0,825 (--)	0,481 (---)	0,570 (---)	0,958 (-+)	0,799 (---)	0,888 (--)	0,853 (--)	0,913 (-)

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