

**ANOMALOUS PROPERTIES OF NMR  $^1\text{H}$  SPECTRA  
OF HALOIDBENZENS  $\text{C}_6\text{H}_5\text{-HAL}$**

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**Abstract.** In a series of monosubstituted benzenes the halogen atoms as substituents worsen correlation dependence of *para*-protons chemical shifts  $\delta_p^{\text{H}}$  on Brown's *para*-constants  $\sigma_p^+$ . So it was suggested to consider halogen atoms as a separate group of substituents. We have introduced for halogen substituents the conception of virtual "spectral Brown's *para*-constants", marked  $\sigma_{p,sp}^+$ . It is suggested that these constants show the maximum capacity of substituents to conjugate with the reaction center. To justify the decision to consider halogen atoms as a separate group of substituents the  $\delta_i^{\text{H}}$  dependences on the number of chemical bonds between the substituent and considered proton were investigated. The anomalous properties of halide atom as substituents are revealed and presented graphically. Also we discuss some other unexplained properties of halogen elements.

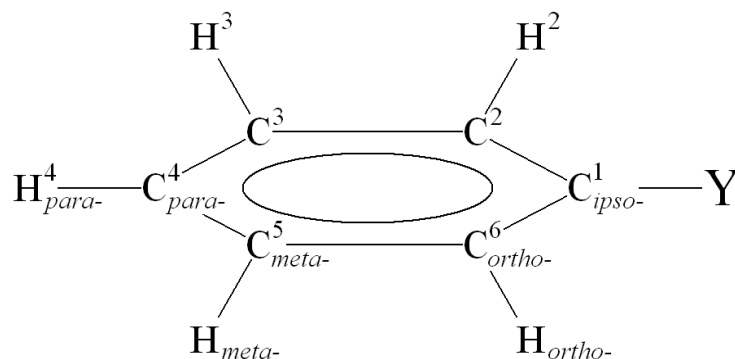
**Keywords:** NMR  $^1\text{H}$  spectra, monosubstituted benzenes, basic and differential spectral parameters, anomalous properties of halide atom as substituents, graphic interpretation of NMR  $^1\text{H}$  spectral parameters of monosubstituted benzenes, "hill" and "pit" shapes of plots, conception of virtual "spectral Brown's *para*-constants"  $\sigma_{p,sp}^+$ .

## 1. Introduction

In the previous report [1] we described the investigation results concerning dependence of phenyl protons chemical shifts ( $\delta_i^{\text{H},\text{N}}$ ) in the NMR  $^1\text{H}$  spectra of **N** monosubstituted benzenes (**N = 1-26**) upon the parameters characterizing the Y substituent nature in the definite chemical reactions, e.g. upon Hammett's constants « $\sigma$ », Brown's constants « $\sigma^+$ », etc. We analyzed 66 equations for  $\delta_i^{\text{H},\text{N}}$  [by 22 for each of three types of phenyl ring protons ( $i = o-, m-, p-$ )] in 25 monosubstituted benzenes (**1-11** and **13-26**) of the general formula  $\text{C}_6\text{H}_5\text{-Y}$  (**N = 26**) containing 25 most prevalent substituent Y, as well as in unsubstituted benzene **12**<sup>1</sup>.

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<sup>1</sup> The substituents choice is stipulated by the presence of maximum quantity of table data of their parameters characterizing the substituent nature; the order of compounds numeration coincides (mainly) with the increase of their Brown's constants.



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where Y = N(CH<sub>3</sub>)<sub>2</sub> (**1**), NH<sub>2</sub> (**2**), OH (**3**), OCH<sub>3</sub> (**4**), OC<sub>6</sub>H<sub>5</sub> (**5**), SCH<sub>3</sub> (**6**), CH<sub>3</sub> (**7**), C<sub>2</sub>H<sub>5</sub> (**8**), i-C<sub>3</sub>H<sub>7</sub> (**9**), t-C<sub>4</sub>H<sub>9</sub> (**10**), C<sub>6</sub>H<sub>5</sub> (**11**), H (**12**), Si(CH<sub>3</sub>)<sub>3</sub> (**13**), F (**14**), Cl (**15**), Br (**16**), I (**17**), CO<sub>2</sub>H (**18**), CO<sub>2</sub>CH<sub>3</sub> (**19**), CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub> (**20**), CF<sub>3</sub> (**21**), CH<sub>3</sub>C=O (**22**), CH=O (**23**), CN (**24**), SO<sub>2</sub>CH<sub>3</sub> (**25**), NO<sub>2</sub> (**26**).

The values of chemical shifts – basic spectral parameters  $\delta_i^{H,N}$  (where “i” denotes the proton type ( $i = o-, m-, p-$ ) and “N” – above-mentioned number of monosubstituted benzene (**1-26**)), as well as values of differential spectral parameters ( $\Delta\delta_i^{H,N}$ ,  $\Delta\delta_{i-j}^{H,N}$ ) are represented in Table 1. The differential parameters  $\Delta\delta_i^{H,N}$  are entered for higher clarity because they represent by themselves the chemical shifts calculated relatively to unsubstituted benzene **12**. These parameters are calculated for each of three types of protons in all compounds **1-26** by the formula:  $\Delta\delta_i^{H,N} = \delta_i^{H,N} - \delta_i^{H,12}$  and may have both positive and negative signs. The differential parameters  $\Delta\delta_{i-j}^{H,N}$  were discussed below.

Table 1

Values of basic ( $\delta_i^{H,N}$ ) and differential ( $\Delta\delta_i^{H,N}$ ,  $\Delta\delta_{i-j}^{H,N}$ ) spectral parameters of monosubstituted benzenes 1-26

No.	Substituent Y	$\delta_i^{H,N}$ , ppm			$\Delta\delta_i^{H,N}$ , ppm			$\Delta\delta_{i-j}^{H,N}$ , ppm	
		$\delta_o^H$	$\delta_m^H$	$\delta_p^H$	$\Delta\delta_o^H$	$\Delta\delta_m^H$	$\Delta\delta_p^H$	$\Delta\delta_{o-m}^{H,N}$	$\Delta\delta_{m-p}^{H,N}$
<b>1</b>	NMe <sub>2</sub>	6.725	7.23	6.71	-0.60	-0.10	-0.62	-0.50	+0.52
<b>2</b>	NH <sub>2</sub>	6.625	7.13	6.73	-0.70	-0.20	-0.60	-0.50	+0.40
<b>3</b>	OH	6.82	7.22	6.92	-0.51	-0.11	-0.41	-0.40	+0.30
<b>4</b>	OMe	6.885	7.27	6.93	-0.44	-0.06	-0.40	-0.38	+0.34
<b>5</b>	OPh	6.995	7.30	7.07	-0.33	-0.03	-0.26	-0.30	+0.23
<b>6</b>	SMe	7.25	7.25	7.11	-0.08	-0.08	-0.22	0.00	+0.14
<b>7</b>	Me	7.15	7.23	7.14	-0.18	-0.10	-0.19	-0.08	+0.09
<b>8</b>	Et	7.18	7.26	7.15	-0.15	-0.07	-0.18	-0.08	+0.09
<b>9</b>	i-Pr	7.215	7.27	7.15	-0.11	-0.06	-0.18	-0.05	+0.12
<b>10</b>	t-Bu	7.385	7.29	7.16	0.06	-0.04	-0.17	+0.10	+0.13
<b>11</b>	Ph	7.57	7.40	7.31	0.24	0.07	-0.02	+0.17	+0.09
<b>12</b>	H	7.33	7.33	7.33	0	0	0	0	0
<b>13</b>	SiMe <sub>3</sub>	7.52	7.33	7.33	0.19	0	0	+0.19	0.00
<b>14</b>	F	7.03	7.31	7.10	-0.30	-0.02	-0.23	-0.28	+0.21

15	Cl	7.32	7.26	7.21	-0.01	-0.07	-0.12	+0.06	+0.05
16	Br	7.48	7.20	7.26	0.15	-0.13	-0.07	+0.28	-0.06
17	I	7.68	7.07	7.30	0.35	-0.26	-0.03	+0.61	-0.23
18	CO <sub>2</sub> H	8.125	7.46	7.60	0.80	0.13	0.27	+0.67	-0.14
19	CO <sub>2</sub> Me	8.035	7.42	7.53	0.71	0.09	0.20	+0.62	-0.11
20	CO <sub>2</sub> Et	8.045	7.42	7.53	0.72	0.09	0.20	+0.63	-0.11
21	CF <sub>3</sub>	7.61	7.46	7.53	0.28	0.13	0.20	+0.15	-0.07
22	Ac	7.95	7.44	7.55	0.62	0.11	0.22	+0.51	-0.11
23	CH=O	7.87	7.52	7.62	0.54	0.19	0.29	+0.35	-0.10
24	CN	7.65	7.47	7.61	0.32	0.14	0.28	+0.18	-0.14
25	SO <sub>2</sub> Me	7.95	7.58	7.67	0.62	0.25	0.34	+0.37	-0.09
26	NO <sub>2</sub>	8.22	7.56	7.71	0.89	0.23	0.38	+0.66	-0.15

The best correlation coefficient (0.966) was found for the dependence ( $\Delta\delta_p^{H,N} - \sigma_p^+$ ), i.e. for the dependence of  $\Delta\delta_p^{H,N}$  *para*-protons on Brown's *para*-constants  $\sigma_p^+$ . While analyzing this graphic dependence it was found [2] that 4 points of haloid compounds **14-17** have the greatest deviation from the straight line built for  $\sigma_p^+$  values being in our disposal (22 points). Due to this deviation the calculated correlation coefficient R decreases. If we consider the haloid atoms as a separate group of substituents then the R value increases to 0.989 for residuary 18 compounds.

Here we make an attempt to logically substantiate the decision [2] concerning consideration of haloid atoms as a separate group of substituents. For the detailed analysis of the investigated spectral parameters  $\delta_i^{H,N}$  and  $\Delta\delta_i^{H,N}$  it is necessary to examine in details the ratio between mentioned values for each of protons three types.

## 2. Experimental

To study the spectra peculiarities of hydrogen atoms nuclei of monosubstituted benzenes **1-26** we used the basic spectral parameters  $\delta_i^H$  described in literature. All values of the basic spectral parameters  $\delta_i^{H,N}$  (and other data) were taken from [1] without changes but rounded till values divisible by 0.01 ppm.

## 3. Results and Discussion

### 3.1. Ortho- and meta-protons

#### 3.1.1. Extreme spectral parameters of monosubstituted benzenes 1-26

Let us consider the extreme values of three types of protons ( $i = o-, m-, p-$ ) for all 26 monosubstituted benzenes. The number of values should be 6: by two values for every type of protons  $i$ . The subscripts "max" and "min" are introduced for their denomination. At the same time the highest (maximum) value  $\delta_{i,max}^H$  and the lowest (minimum) value  $\delta_{i,min}^H$  do not contain symbol "N" in superscript. Every extreme value is characterized by the differential parameters

relatively to benzene; at that the compound number is introduced into superscript. The positive by sign (maximum) extreme differential parameters are denoted as  $\Delta\delta_{i,\max}^{\text{H,N}}$ , and negative ones – as  $\Delta\delta_{i,\min}^{\text{H,N}}$ . They are calculated by the formulae:  $\Delta\delta_{i,\max}^{\text{H,N}} = \delta_{i,\max}^{\text{H}} - \delta_i^{\text{H,12}} = \delta_{i,\max}^{\text{H}} - 7.33$  ppm;  $\Delta\delta_{i,\min}^{\text{H,N}} = \delta_{i,\min}^{\text{H}} - \delta_i^{\text{H,12}} = \delta_{i,\min}^{\text{H}} - 7.33$  ppm.

It is logical to assume that maximum values of every three basic parameters  $\delta_{i,\max}^{\text{H}}$  (hence, differential parameters  $\Delta\delta_{i,\max}^{\text{H,N}}$  also) should belong to monosubstituted benzenes with the strongest electron-accepting substituents Y: nitrogroup in nitrobenzene **26** or methylsulphonyl group in methylsulphone **25**. Similarly, the minimum parameters  $\delta_{i,\min}^{\text{H}}$  ( $\Delta\delta_{i,\min}^{\text{H,N}}$ ) may be expected for the compounds with the strongest electron-donating aminogroups – N,N-dimethylaniline **1** or aniline **2**. Actually, our assumptions were justified except meta-protons of iodobenzene **17**. For *ortho*-protons the same extreme differential parameters are:  $\delta_{o,\max}^{\text{H}} = 8.22$ ;  $\Delta\delta_{o,\max}^{\text{H,N}} = \Delta\delta_o^{\text{H,26}} = 8.22 - 7.33 = +0.89$  ppm; and  $\delta_{o,\min}^{\text{H}} = 6.63$  ppm;  $\Delta\delta_{o,\min}^{\text{H,N}} = \Delta\delta_o^{\text{H,2}} = 6.63 - 7.33 = -0.70$  ppm. For *meta*-protons:  $\delta_{m,\max}^{\text{H}} = 7.58$  ppm;  $\Delta\delta_{m,\max}^{\text{H,N}} = \Delta\delta_m^{\text{H,25}} = +0.25$  ppm; and  $\delta_{m,\min}^{\text{H}} = 7.07$  ppm,  $\Delta\delta_{m,\min}^{\text{H,N}} = \Delta\delta_m^{\text{H,17}} - 0.26$  ppm. For *para*-protons:  $\delta_{p,\max}^{\text{H}} = 7.71$  ppm;  $\Delta\delta_{p,\max}^{\text{H,N}} = \Delta\delta_p^{\text{H,26}} = +0.38$  ppm; and  $\delta_{p,\min}^{\text{H}} = 6.61$  ppm;  $\Delta\delta_{p,\min}^{\text{H,N}} = \Delta\delta_p^{\text{H,1}} = -0.62$  ppm.

Unexpectedly it was found that in the case of meta-protons the representative of haloidbenzenes – iodobenzene **17** – has the minimum parameter ( $\delta_{m,\min}^{\text{H}} = \delta_m^{\text{H,17}} = 7.07$  ppm) but we expected it would be aniline **1** or dimethylaniline **2** derivative. This expected parameter is only the second minimum ( $\delta_m^{\text{H,2}} = 7.13$  ppm). Such noteworthy fact we'll discuss below. Since the haloidbenzenes **14-17** will be discussed separately, we assume the “second minimum” parameter  $\Delta\delta_m^{\text{H,2}} = -0.20$  ppm of aniline **2** as a minimum parameter  $\Delta\delta_{m,\min}^{\text{H,N}}$ , necessary for the further calculations.

The difference between maximum  $\delta_{i,\max}^{\text{H}}$  and minimum  $\delta_{i,\min}^{\text{H}}$  values of  $\delta_i^{\text{H,N}}$  parameter for protons of every type we denote as differential parameters  $\Delta\delta_{i,\max}^{\text{H}}$ , without symbol “N” in the superscript (in contrast to the above-mentioned parameter  $\Delta\delta_{i,\max}^{\text{H,N}}$ ). This difference is determined by the sum of differential parameters  $\Delta\delta_{i,\max}^{\text{H,N}}$  and  $\Delta\delta_{i,\min}^{\text{H,N}}$  absolute values, i.e.:  $\Delta\delta_{i,\max}^{\text{H}} = |\Delta\delta_{i,\max}^{\text{H,N}}| + |\Delta\delta_{i,\min}^{\text{H,N}}|$ . The value  $\Delta\delta_{o,\max}^{\text{H}}$  for *ortho*-protons ( $\Delta\delta_{o,\max}^{\text{H}}$ ) is higher than those for *meta*- ( $\Delta\delta_{m,\max}^{\text{H}}$ ) and *para*-protons ( $\Delta\delta_{p,\max}^{\text{H}}$ ).  $\Delta\delta_{o,\max}^{\text{H}}$  is almost equal to 1.60 ppm ( $0.89 + 0.70 = 1.59$  ppm). The lowest value was found for *meta*-protons ( $\Delta\delta_{m,\max}^{\text{H}} = 0.25 + 0.20 = 0.45$  ppm). For *para*-protons the parameter  $\Delta\delta_{p,\max}^{\text{H}}$  is intermediate by its value ( $0.38 + 0.62 = 1.00$  ppm).

The symmetry of extreme points relative to “zero line” of benzene **12** for *ortho*-, *meta*- and *para*-protons is characterized by the ratio between absolute values of extreme parameters  $|\Delta\delta_{i,\max}^{\text{H,N}}|$  and  $|\Delta\delta_{i,\min}^{\text{H,N}}|$ . If the ratio is closer to one the extreme points are more symmetrical. The closest points of *meta*-protons as well as the most distant ones of *ortho*-protons are the most symmetrical parameters. The ratios between them are:  $|\Delta\delta_{m,\max}^{\text{H,N}}| / |\Delta\delta_{m,\min}^{\text{H,N}}| = 0.25 / 0.20 = 1.25$ , and  $|\Delta\delta_{o,\max}^{\text{H,N}}| / |\Delta\delta_{o,\min}^{\text{H,N}}| = 0.89 / 0.70 = 1.27$ . In both cases the absolute values of upper segments ( $|\Delta\delta_{m,\max}^{\text{H,N}}|$  and  $|\Delta\delta_{o,\max}^{\text{H,N}}|$ ) are higher than those of lower segments ( $|\Delta\delta_{m,\min}^{\text{H,N}}|$  and  $|\Delta\delta_{o,\min}^{\text{H,N}}|$ ), respectively). The opposite situation is for the least symmetrical *para*-protons: the maximum differential parameter  $\Delta\delta_{p,\max}^{\text{H}} = 0.38$  ppm is considerably lower than minimum parameter  $\Delta\delta_{p,\min}^{\text{H}} = 0.62$  ppm and their ratio (or rather its reciprocal  $0.62/0.38 = 1.63$ ) is

considerably higher than above-mentioned ratio for ortho- and meta-protons. During the results discussion we try to explain this phenomenon.

### 3.1.2. Graphic interpretation of NMR<sup>1</sup>H spectral parameters of monosubstituted benzenes.

Let us plot the dependence of all three types of phenyl protons (values  $\Delta\delta_i^{H,N}$ ) on the number of chemical bonds (n) between the substituent Y and examined proton. Then we'll analyze the plots of the group consisting of 4 haloidaryl compounds **14-17**.

#### 3.1.2.1. Plot structure

The number of chemical bonds between the substituent Y and *ortho*-protons equals to 3: Y-C<sub>ipso</sub>-C<sub>ipso</sub>-C<sub>ortho</sub> and C<sub>ortho</sub>-H<sub>ortho</sub> (or Y-C<sup>1</sup>; C<sup>1</sup>-C<sup>2</sup>; C<sup>2</sup>-H<sup>2</sup>). There are 4 bonds for meta-protons and 5 – for para-protons. Correspondingly, numbers n at abscissa are 3, 4 and 5. While connecting the point corresponding to the basic parameter  $\delta_o^{H,N}$  (at n=3) with the point of parameter  $\delta_m^{H,N}$  (at n=4) by vector straight line, we obtain the left branch of the plot. We plot the right branch of the plot in the same way connecting the point  $\delta_m^{H,N}$  (at n=4) with the point  $\delta_p^{H,N}$  (at n=5). The left branch projection to ordinate axe is also a vector (i.e. it has the corresponding sign) and equal to the new introduced differential spectral parameter denoted as  $\Delta\delta_{o-m}^{H,N}$ , i.e. the difference between the initial basic spectral parameters:  $\Delta\delta_{o-m}^{H,N} = \delta_o^{H,N} - \delta_m^{H,N}$ . Similarly, the right branch projection is denoted by differential parameter  $\Delta\delta_{m-p}^{H,N}$ , equal to:  $\Delta\delta_{m-p}^{H,N} = \delta_m^{H,N} - \delta_p^{H,N}$ . The values of differential spectral parameter named as  $\Delta\delta_{i-j}^{H,N}$  are also represented in Table 1.

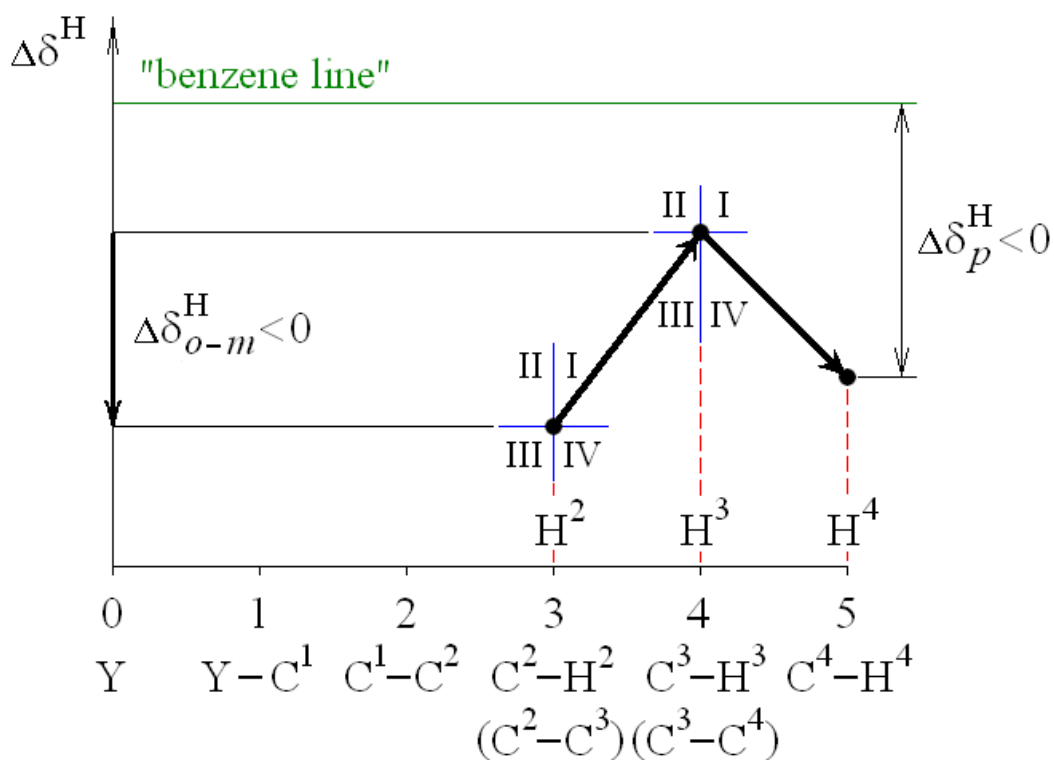
Each of two branches may be “abrupt” or “flat” or parallel to abscissa. The line “slope” is a qualitative characteristics<sup>2</sup> and depends upon the absolute values of  $|\Delta\delta_{o-m}^{H,N}|$  parameter for the left branch and  $|\Delta\delta_{m-p}^{H,N}|$  parameter – for the right. For the greater value the slope is more abrupt.

#### 3.1.2.2. Types of plots

Combining different signs of the differential parameters  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$  (if they are not equal to zero) 4 main types of plots are possible. Three of them are represented in Figs. 1-3. Plots 1 and 2 represent the cases when the parameters  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$  have different signs. Each branch of the plots is situated in one of two quadrants: in the first or in the forth. Thus, in Fig. 1 (the parameter  $\Delta\delta_{o-m}^{H,N} < 0$ , and the parameter  $\Delta\delta_{m-p}^{H,N} > 0$ , see table 1) the left branch is situated in the first quadrant and the right branch – in the forth one.

<sup>2</sup> “Pace”, i.e. the distance between two nearest points along abscissa is an arbitrary value depending on aesthetic preference of the authors. Therefore the slope angle at the given plots depending on “rate” has not physical sense and is not calculated.

Fig. 1



The plot 2 (Fig. 2) is plotted for the opposite case, when  $\Delta\delta_{o-m}^{H,N} > 0$ , and  $\Delta\delta_{m-p}^{H,N} < 0$ . Pro tanto, the left branch is situated in the fourth quadrant and the right branch – in the first one.

Fig. 2

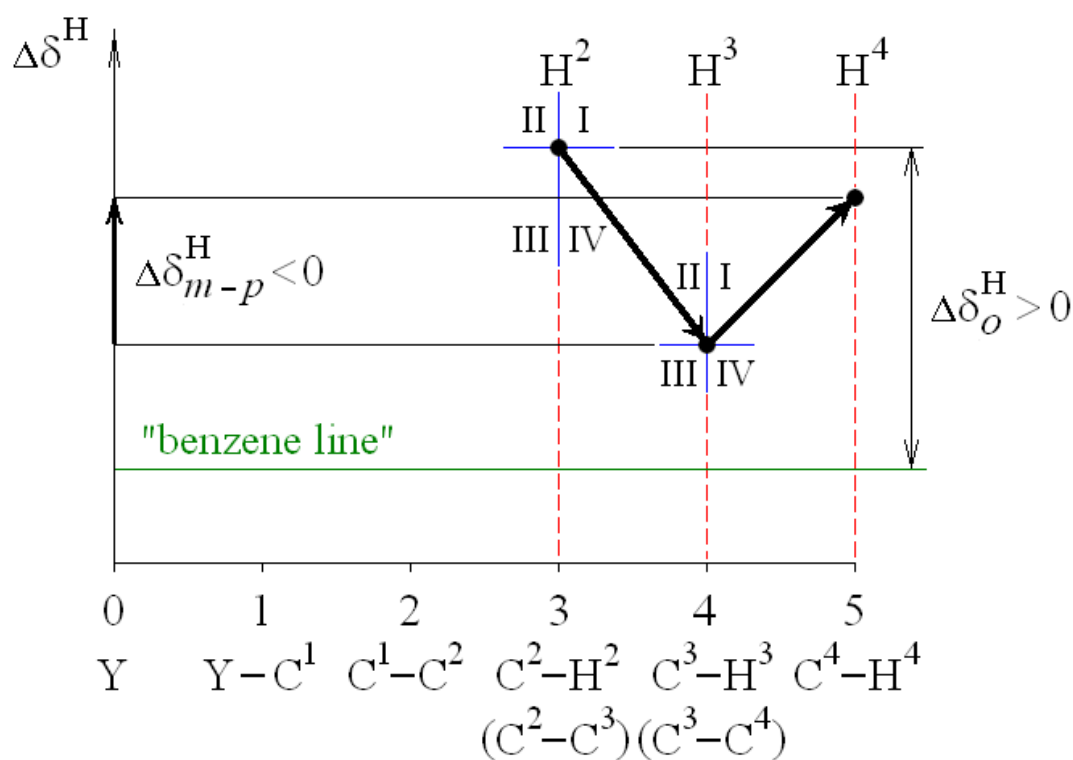
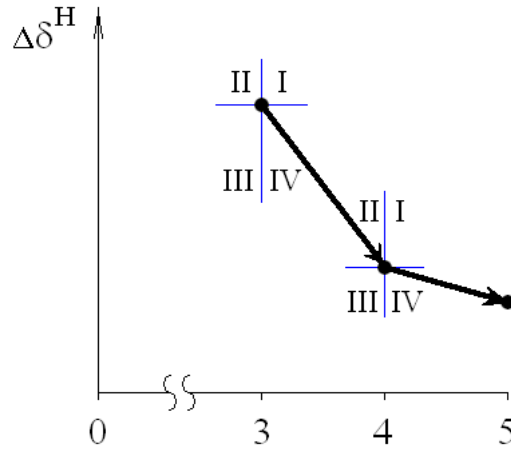


Fig. 3 represents the case when the parameters  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$  have the same sign ("plus"), i.e.  $\Delta\delta_{o-m}^{H,N} > 0$ , and  $\Delta\delta_{m-p}^{H,N} > 0$ . Both branches of this plot are situated in the fourth quadrant.

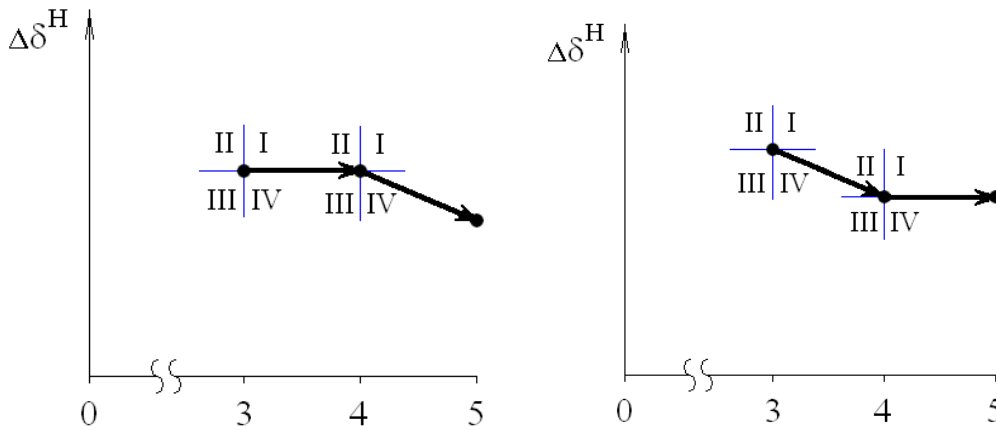
Fig. 3



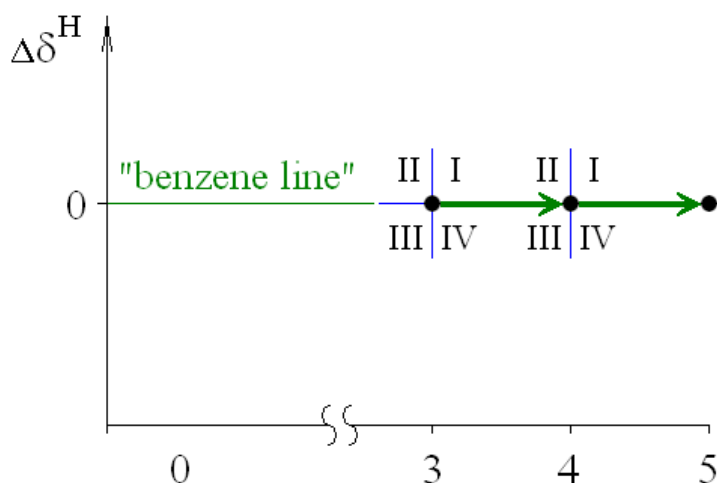
If  $\Delta\delta_{o-m}^{H,N} < 0$ , and  $\Delta\delta_{m-p}^{H,N} < 0$ , both branches are situated in the first quadrant. This variant is not given in the Fig.

If  $\Delta\delta_{o-m}^{H,N}$  or  $\Delta\delta_{m-p}^{H,N}$  is equal to zero, another 4 types of plots are possible (two of them are represented in Figs. 4 and 5). Fig. 4 represents the case when  $\Delta\delta_{o-m}^{H,N} = 0$ , and  $\Delta\delta_{m-p}^{H,N} < 0$ ; Fig. 5 – when  $\Delta\delta_{o-m}^{H,N} > 0$ , and  $\Delta\delta_{m-p}^{H,N} = 0$ .

Figs. 4,5



The last ninth variant of the ratio between  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$ , when  $\Delta\delta_{o-m}^{H,N} = 0 = \Delta\delta_{m-p}^{H,N}$  is represented in Fig. 6. Both branches of the plot are straight lines coincident with the abscissa.



The plot in Fig. 6 is the plot for benzene **12** ( $Y=H$ ), because  $\delta_o^{H,12} = \delta_m^{H,12} = \delta_p^{H,12} = 7.33$  ppm and  $\Delta\delta_{o-m}^{H,N} = \Delta\delta_{m-p}^{H,N} = 0$ , correspondingly. Each of 25 plots for other compounds is a broken line consisting of two sloping branches which cross in the point determined by the chemical shift of meta-protons ( $n=4$ ). Every plot corresponds to the one of 8 above-mentioned variants of the ratio between  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$ . These plots are represented schematically in Figs. 1-6. It should be noted that the **majority of plots (18) corresponds to the first two variants**, therefore we consider them as typical ones (most of them were shown in Fig. 7).

### 3.1.2.3. Plots of the compounds 1-11 with electron-donating substituents

For the majority of compounds **with electron-donating substituents Y (1-11)**<sup>3</sup> the ordinary type of plot corresponds to the 1 type (Fig. 1). Thus for the compounds with the strongest electron-repellent substituents - aminogroups: N,N-dimethylaniline **1** [ $Y = N(CH_3)_2$ ] and aniline **2** ( $Y = NH_2$ ), we obtained the plots with the most abrupt branches presented in the bottom part of Fig. 7. The absolute values of their parameters  $|\Delta\delta_{o-m}^{H,N}|$  and  $|\Delta\delta_{m-p}^{H,N}|$  (where  $N = 1$  or  $2$ ) are equal to 0.40–0.50 ppm. For the above-situated plots of phenol **3** and its ethers **4** and **5** with weaker electron-donating groups ( $Y=OH$  and  $Y=OR$ ) both branches are more flat ( $|\Delta\delta_{o-m}^{H,N}|$  and  $|\Delta\delta_{m-p}^{H,N}| \sim 0.30 - 0.40$  ppm). The plot branches of other "intermediate" alkylbenzenes are still more flat (Fig. 7). The transition takes place from dimethylaniline **1** with the most strong electro-donating group to "neutral" benzene **12**: toluene **7**, ethylbenzene **8** and cumene **9** containing "medium" by strength electron-donating alkyl groups  $Y$  ( $|\Delta\delta_{o-m}^{H,N}|$  and  $|\Delta\delta_{m-p}^{H,N}| \sim 0.05 - 0.10$  ppm). Let us note that the plot of fluorobenzene **14** (represented also in Fig. 7 but discussed below) is situated between the plots of diphenyl ether **5** and toluene **7**. The remaining three compounds with electron-donating substituents  $Y$  (**6, 10 and 11**) have other types of plots given in Figs. 3.

<sup>3</sup> Trimethylsilyl group [ $Y=Si(CH_3)_3$ ] in trimethylphenylsilane **13** we refer to neither electron-donating nor electron-accepting substituents. Its constants characterizing the substituent are almost equal to zero (but Hammett's constant is positive and Braun's constant is negative). Three from four differential parameters of the compound **13** are equal to zero ( $\Delta\delta_m^{H,13} = \Delta\delta_p^{H,13} = \Delta\delta_{m-p}^{H,13} = 0$ ). Therefore the ideal plot (see below) of silane **13** coincides with "benzene line" (i.e. "zero line" of unsubstituted benzene **12**) and will not be discussed further.



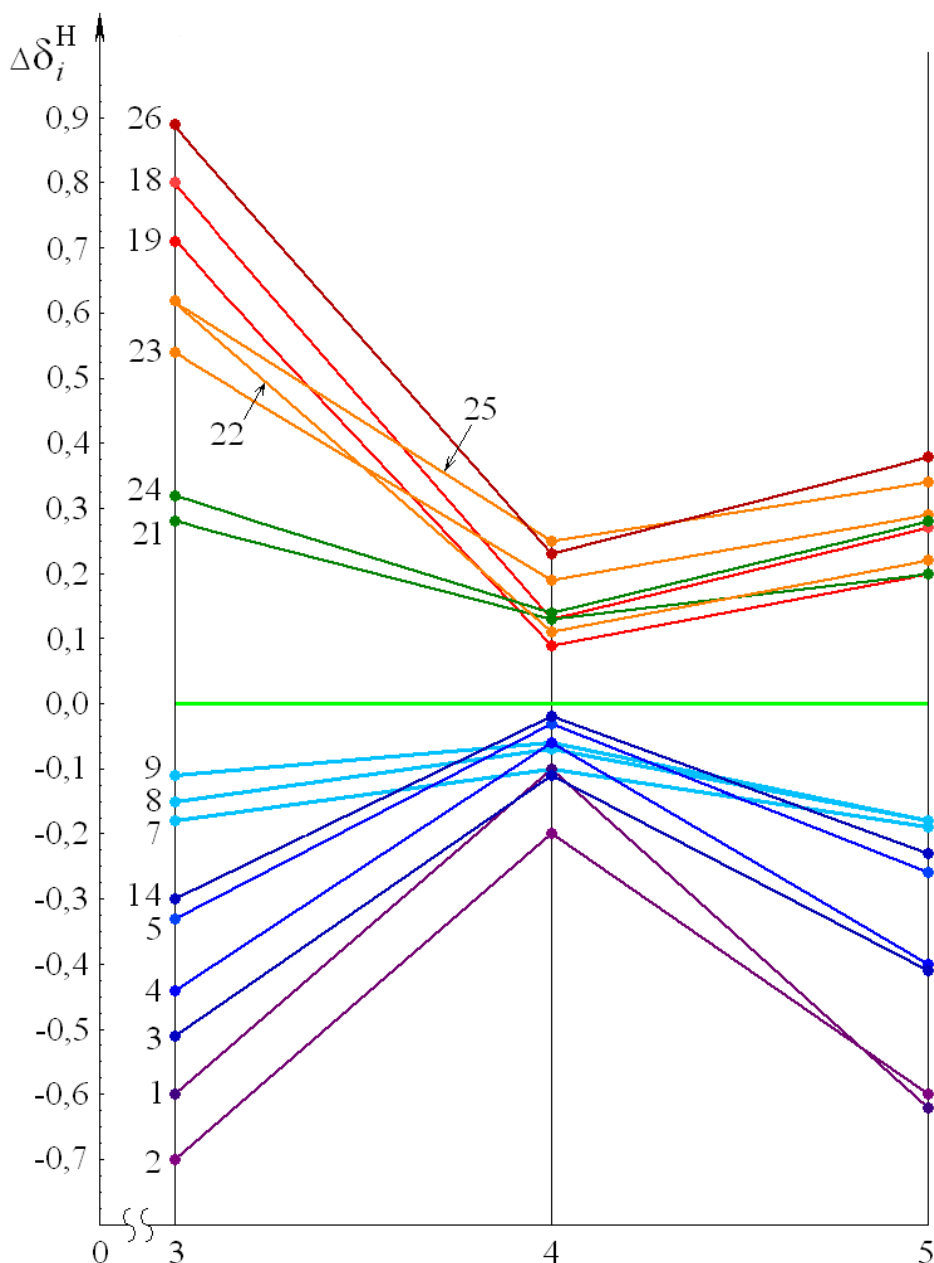
### 3.1.2.4. Plots of the compounds 18-26 with electron-accepting substituents

The plots of monosubstituted benzenes with electron-accepting substituents Y (**18-26**) are also represented in the upper part of Fig. 7 and correspond to the variant 2 (Fig. 2). Moreover, nitrobenzene **26** with the most strong electron-accepting nitrogroup (Y=NO<sub>2</sub>) presents the topmost plot with abrupt branches ( $|\Delta\delta_{o-m}^{H,N}| = 0.66$  ppm,  $|\Delta\delta_{m-p}^{H,N}| = 0.15$  ppm). The branches of other 8 compounds (**18-25**) are situated more flat, except left branch of benzoic acid **18** ( $|\Delta\delta_{o-m}^{H,N}| = 0.67$  ppm).

### 3.1.2.5. Typical plots

The plots consisting of the most “abrupt branches” look like a high hill (anilines **1** and **2**) or an unsymmetrical deep pit (nitrobenzene **26**). The plots of other “intermediate” compounds are more flat and look like a flat hill or a shallow pit. It should be stressed that **all “pit” plots are situated above the benzene line and all “hill” plots – under the line.**

Thus, 19 from 26 plots of monosubstituted benzenes painted in different colors (including non-substituted benzene C<sub>6</sub>H<sub>6</sub> painted bright green) are represented in Fig. 7 and more or less similar to the “typical” variants presented in Figs. 1 and 2. “The highest hill” is observed for aniline **1** and **2** derivatives and “the deepest pit” – for nitrobenzene **26**. Moreover, its plot is one of the most asymmetric ones (relative to the vertical line passed through the point of meta-protons at n=4), because the left descending branch is much more abrupt than the right ascending branch. At the same time the “hills” of anilines **1** and **2** are almost symmetric because absolute values of their parameters  $|\Delta\delta_{o-m}^{H,N}|$  and  $|\Delta\delta_{m-p}^{H,N}|$  are close.



### 3.1.2.6. Atypical plots

Three of the remaining 7 “atypical” plots [where  $Y = \text{Bu}^t$  (**10**),  $\text{Ph}$  (**11**) and  $\text{Cl}$ (**15**)] have branches as slope lines but there is not transition of broken line into other quadrant in the point of intersection. In all three cases the parameters  $\Delta\delta_{o-m}^{\text{H,N}}$  and  $\Delta\delta_{m-p}^{\text{H,N}}$  have the same sign «+» (i.e. both  $\Delta\delta_{o-m}^{\text{H,N}} > 0$ , and  $\Delta\delta_{m-p}^{\text{H,N}} > 0$ ). Therefore, both branches of the plot are situated in the forth quadrant and correspond to the type represented in Fig. 3. What’s concerning two of the remaining 4 “atypical” plots? The left branch in toianisole **6** and right one in phenyltrimethylsilane **13** are not slope lines but are parallel to the abscissa. They correspond to those two variants depicted in Figs. 4 and 5.

The last two plots belong to haloidbenzenes [ $Y = \text{Br}$  (**16**) и  $\text{I}$  (**17**)]. They correspond to none from 9 above-mentioned variants. Therefore they are presented separately in Figs. 14 and 15 (see below). **By their shapes** they are similar to the “pit” plot of nitrobenzene **26** (Fig. 2) but they are

considerably deeper. **Their point of intersection** ( $n=4$ ) is situated **below the benzene line** in contrast to the “pits” of the compounds **18-26**. The deepest pit is observed for iodobenzene **17**.

### **3.1.3. The analysis of the compounds 1-26 plots**

#### **3.1.3.1. Virtual plots**

To analyze the haloidbenzenes **14-17** plots it is necessary to examine the ratio between parameters of every two branches in other plots, or rather quantitative ratio of their projections onto ordinate axe (i.e. the parameters  $\Delta\delta_{o-m}^{H,N}$  and  $\Delta\delta_{m-p}^{H,N}$ ).

##### **3.1.3.1.1. Ideal plots of the compounds 1-11 with electron-donating substituents**

In the bottom part of Fig. 7 there are plots of the compounds with electron-donating substituents Y. As we move bottom-up from “abrupt hill” (aniline **1** and **2** derivatives with strong electron-repellent substituents – amino groups) to the “plain” of “neutral” benzene **12** we observe the gradual “flattening” of every next “hill” and the transition of last “low hill” (cumene **9**) into the “plain” of benzene **12**. At the same time some resemblance to plots is preserved.

Let us note that during the transition of bottom plot to the upper one there is a **gradual unidirectional increase of all three parameters**  $\Delta\delta_i^{H,N}$  (i.e. the decrease of absolute values of their negative magnitudes) but the **rates of increase are different**. Actually due to the non-proportional change (increase or decrease) of the parameters  $\Delta\delta_o^{H,N}$  and  $\Delta\delta_m^{H,N}$  one or two branches of both plots intersect sometimes (see for instance plot left branches of dimethylaniline **1** and phenol **3** or right branches of dimethylaniline **1** and aniline **2**, as well as other examples given in Fig. 7).

Let us consider the **ideal case** when during gradual (step-by-step) transition from the “high hill” (aniline **2**) to the “low hill” (e.g. cumene **9**) the proportion of parameters  $\Delta\delta_i^{H,N}$  increase is preserved. We denote such parameters as virtual “proportional differential parameters”  $\Delta\delta_{i,pr}^{H,N}$ . We call them “ideal proportional parameters”. The values of para-protons parameters  $\Delta\delta_p^{H,N}$  (Table 1) we accepted as **invariable basis**, i.e.  $\Delta\delta_p^{H,N} = \Delta\delta_{p,pr}^{H,N}$ . The para-parameters are chosen due to the best coefficient of linear correlation for Brown’s para-constants  $\sigma_p^+$ . Then in order to preserve the proportions, the expected increase at every transition step (i.e. the expected decrease by absolute value of negative by sign) of two “ideal proportional” parameters  $\Delta\delta_{o,pr}^{H,N}$  and  $\Delta\delta_{m,pr}^{H,N}$  would be **proportional** to the increase of the parameter  $\Delta\delta_{p,pr}^{H,N} = \Delta\delta_p^{H,N}$ . It means, **virtual “proportional differential parameters” are calculated for those ideal cases when the chemical shifts of ortho- and meta-protons would be proportional to the values of para-protons chemical shifts.**

Obviously that the greatest changes of the absolute value takes place for ortho-protons  $\Delta\delta_{o,pr}^{H,N}$ , and the least changes – for meta-protons  $\Delta\delta_{m,pr}^{H,N}$ . For medium changes the para-parameters  $\Delta\delta_p^{H,N} = \Delta\delta_{p,pr}^{H,N}$  are the basis. As we approach the “benzene line”, the every next plot is “flattened”; at the same time the branches of neighbor plots do not intersect and the resemblance of plots (see Fig. 8 represented below) is preserved (as far as possible).

The coefficient of change proportionality of the “ideal proportional” parameters  $\Delta\delta_{o,pr}^{H,N}$  or  $\Delta\delta_{m,pr}^{H,N}$  of the investigated compound **N** with electron-donating substituent (**N=1-11**) we denote as  $k_N$  and determine as a ratio of its para-parameter  $\Delta\delta_p^{H,N}$  to the parameter  $\Delta\delta_p^{H,N,standard}$  of standard compound. As a standard it is advisable to choose a compound with extreme (in our case – with minimum) parameter  $\Delta\delta_{p,min}^H$ , in order all coefficients  $k_N$  should be less than one. The value of coefficients  $k_N$  may be considered as **qualitative** characteristics of the electron-donating strength of the substituent Y.

We chose aniline **2** as the standard. Its para-parameter  $\Delta\delta_p^{H,2} = \Delta\delta_{p,min}^H = -0.60$  ppm is the second of two least (extreme) values of para-parameters  $\Delta\delta_p^{H,N}$  (see above). The reasons of such choice we discuss below. Then for example, for cumene **9** the coefficient  $k_N$  is equal to:  $k_9 = \Delta\delta_p^{H,9} / \Delta\delta_p^{H,N,standard} = (-0.18) / (-0.60) = 0.30$ . To preserve the resemblance of “ideal plots” the values of the parameters  $\Delta\delta_{o,pr}^{H,N}$  and  $\Delta\delta_{m,pr}^{H,N}$  are calculated by the formula:  $\Delta\delta_{i,pr}^{H,N} = k_N \cdot \Delta\delta_{i,min}^{H,N}$ . For cumene **9** (see Table 2) they are as following: *ortho-protons*:  $\Delta\delta_{o,pr}^{H,9} = 0.30 \cdot (-0.70) = -0.21$  ppm; *meta-protons*  $\Delta\delta_{m,pr}^{H,9} = 0.30 \cdot (-0.20) = -0.06$  ppm. Only for N,N-dimethylaniline **1** [Y = N(CH<sub>3</sub>)<sub>2</sub>] the coefficient of proportionality exceeds one ( $k_N = 1.03$ ).

We introduce the concept of **virtual “basic proportional parameters”** and denote them as  $\delta_{o,pr}^{H,N}$  and  $\delta_{m,pr}^{H,N}$ . They are equal to the algebraic sum of benzene chemical shift and “proportional differential parameters”  $\Delta\delta_{o,pr}^{H,N}$  or  $\Delta\delta_{m,pr}^{H,N}$ . It means:  $\delta_{o,pr}^{H,N} = 7.33$  ppm +  $\Delta\delta_{o,pr}^{H,N}$ ;  $\delta_{m,pr}^{H,N} = 7.33$  ppm +  $\Delta\delta_{m,pr}^{H,N}$ . For cumene **9** we obtained the following calculated “virtual” values of the “basic proportional parameters”:  $\delta_{o,pr}^{H,9} = 7.33$  ppm – 0.21 = 7.12 ppm (instead of the real value  $\delta_o^{H,9} = 7.22$  ppm, Table 1) and  $\delta_{m,pr}^{H,9} = 7.33$  ppm – 0.06 = 7.27 ppm, corresponding to the real value  $\delta_m^{H,9} = 7.27$  ppm given in Table 1.

### 3.1.3.1.2. Ideal plots of the compounds 18-26 with electron-acceptor substituents

The same situation (by mirror reflection) should take place for 9 “typical” plots of the compounds **N** with electron-accepting substituents (**18-26**), i.e. at “step-by-step” top-down transition from nitrobenzene **26** to benzene **12**. They are depicted in the upper part of Fig. 7. We used the same approach concerning the proportionality of the calculated ortho- ( $\delta_{o,pr}^{H,N}$ ) and meta- ( $\delta_{m,pr}^{H,N}$ ) parameters relative to constant values of para-parameters  $\delta_p^{H,N}$ . To calculate the proportionality coefficient we used benzonitrile **24** with  $\Delta\delta_p^{H,24} = +0.28$  ppm as the standard instead of nitrobenzene **26** with maximum parameter  $\Delta\delta_{p,max}^H = \Delta\delta_p^{H,26} = +0.38$  ppm. The reasons are discussed below. In such a case for three compounds (**23**, **25** and **26**) the coefficients  $k_{23}$ ,  $k_{25}$  and  $k_{26}$  exceeds one (see Table 2).

#### 3.1.3.1.3. The reasons for standard choice

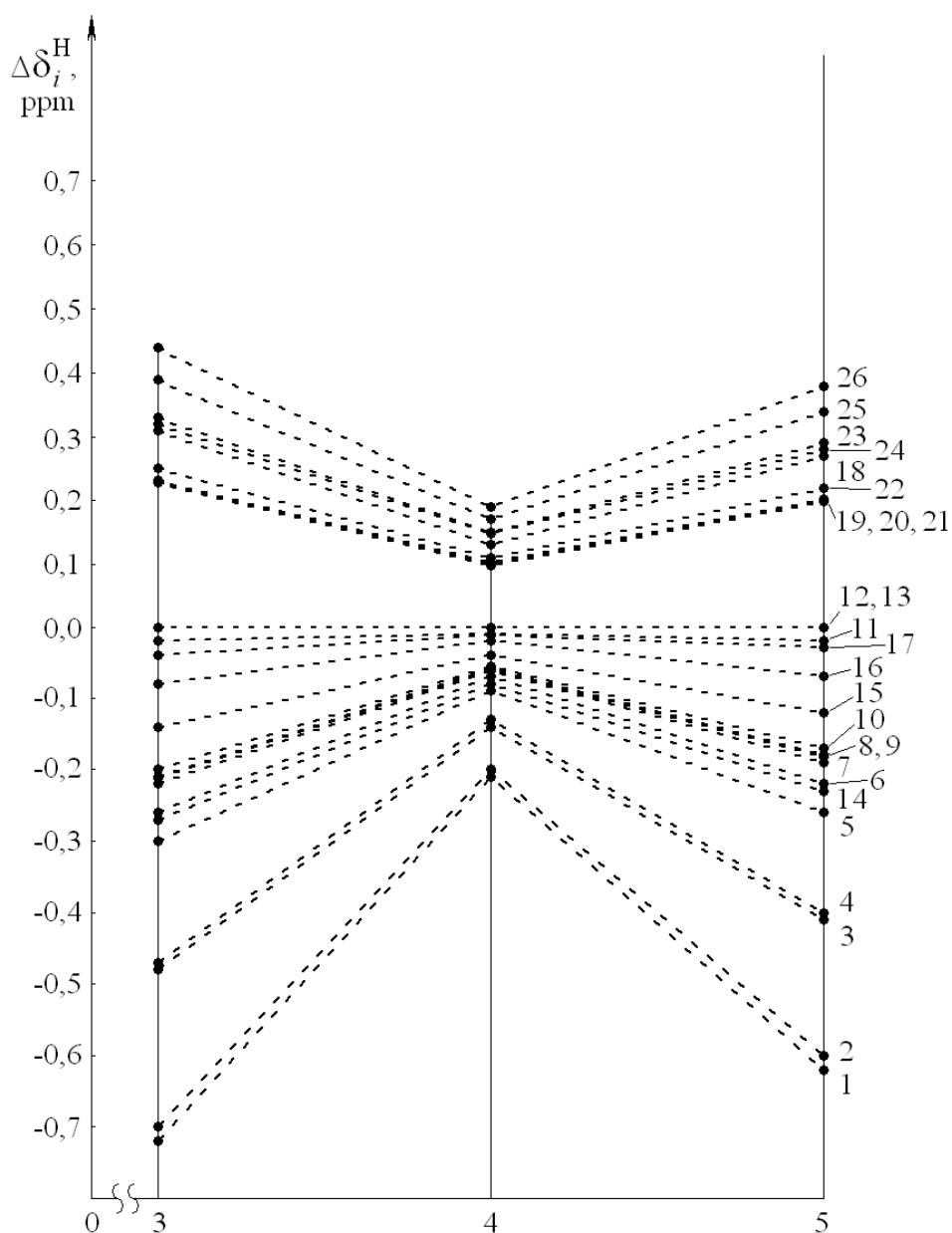
The choice of aniline **2** instead of N,N-dimethylaniline **1** with extreme value of  $\Delta\delta_{p,min}^H$  as the standard for the compounds with electron-donor groups **1-11** is stipulated by the fact that aniline **2** has extreme (minimum) values of ortho- ( $\Delta\delta_{o,min}^H = \Delta\delta_o^{H,2} = -0.70$  ppm) and meta- ( $\Delta\delta_{m,min}^H = \Delta\delta_m^{H,2} = -0.20$  ppm, see above) parameters. The values of para-parameters **1** and **2** are close ( $\Delta\delta_p^{H,1} = -0.62$  ppm and  $\Delta\delta_p^{H,2} = -0.60$  ppm). It is more important that the both branches of

aniline plot are situated almost symmetrically relative to the vertical line passed through the point of meta-protons (at  $n = 4$ ), i.e.  $|\Delta\delta_{o-m}^{H,2}| = 0.50$  ppm and  $|\Delta\delta_{m-p}^{H,N}| = 0.40$  ppm.

The symmetry was the main reason to choose benzonitrile **24** as the standard for  $k_N$  calculations of the compounds with electron-acceptor substituents **18-26**. The plot of benzonitrile is almost symmetrical contrary to nitrobenzene **26** (the plot of which is the most asymmetrical).

The symmetry of aniline **2** and benzonitrile **24** plots is high:  $|\Delta\delta_{o-m}^{H,2}| / |\Delta\delta_{m-p}^{H,2}| = 0.50 / 0.40 = 1.25$ , and ratio  $|\Delta\delta_{o-m}^{H,24}| / |\Delta\delta_{m-p}^{H,24}| = 0.18 / 0.14 = 1.29$ . These proportions are preserved during the construction of "ideal proportional" plots given in Fig. 8 as black dotted lines.

Fig. 8



Let us compare them by contrast with asymmetrical real plot of nitrobenzene **26**, where  $|\Delta\delta_{o-m}^{H,26}| / |\Delta\delta_{m-p}^{H,26}| = 0.65 / 0.15 = 4.33$  (Fig. 11, see below).

### 3.1.3.1.4. The results of calculations

The calculated values of proportionality coefficients  $k_N$ , “proportional differential parameters”  $\Delta\delta_{o,pr.}^{H,N}$  and  $\Delta\delta_{m,pr.}^{H,N}$  and values of virtual chemical shifts of ortho- and meta-protons  $\delta_{o,pr.}^{H,N}$  and  $\delta_{m,pr.}^{H,N}$  for the compounds **1-26** are represented in Table 2. There are also the differences between the real values of the parameters  $\delta_o^{H,N}$  or  $\delta_m^{H,N}$  and their calculated “proportional” values  $\delta_{o,pr.}^{H,N}$  or  $\delta_{m,pr.}^{H,N}$ . These values are placed in brackets and denoted as  $\Delta\Delta\delta_{i,pr.}^{H,N}$ . The differences may also be calculated from the differential parameters, hence:  $\delta_i^{H,N} - \delta_{i,pr.}^{H,N} = \Delta\Delta\delta_{i,pr.}^{H,N} = \Delta\delta_i^{H,N} - \Delta\delta_{i,pr.}^{H,N}$ .

Table 2

The values of the basic parameters  $\delta_i^{H,N}$ , virtual “basic proportional parameters”  $\delta_{i,pr.}^{H,N}$  and their differences ( $\Delta\Delta\delta_{i,pr.}^{H,N}$ ), as well as “differential proportional parameters”  $\Delta\delta_{i,pr.}^{H,N}$

No.	Substituent Y	Para-protons		Coef. $k_N$	Ortho-protons				Meta-protons				Differential parameters	
		$\Delta\delta_p^{H,N}$ , ppm	$\Delta\delta_{p,pr.}^{H,N}$ , ppm		$\Delta\delta_{o,pr.}^{H,N}$ , ppm	$\delta_o^{H,N}$ , ppm	$\delta_{o,pr.}^{H,N}$ , ppm	$\Delta\Delta\delta_{o,pr.}^{H,N}$ , ppm	$\Delta\delta_{m,pr.}^{H,N}$ , ppm	$\delta_m^{H,N}$ , ppm	$\delta_{o,pr.}^{H,N}$ , ppm	$\Delta\Delta\delta_{m,pr.}^{H,N}$ , ppm	$\delta_{o-m,pr.}^{H,N}$ , ppm	$\Delta\delta_{m-p,pr.}^{H,N}$ , ppm
1	NMe <sub>2</sub>	6.71	-0.62	1.03	-0.72	6.73	6.61	(+0.12)	-0.21	7.23	7.12	(+0.11)	-0.51	+0.41
2	NH <sub>2</sub>	6.73	-0.60	1.00	-0.70	6.63	6.63	0.00	-0.20	7.13	7.13	0.00	-0.50	+0.40
3	OH	6.92	-0.41	0.68	-0.48	6.82	6.85	(-0.03)	-0.14	7.22	7.19	(+0.03)	-0.34	+0.27
4	OMe	6.93	-0.40	0.67	-0.47	6.89	6.86	(+0.03)	-0.13	7.27	7.20	(+0.07)	-0.34	+0.27
5	OPh	7.07	-0.26	0.43	-0.30	7.00	7.03	(+0.03)	-0.09	7.30	7.24	(+0.06)	-0.21	+0.17
6	SMe	7.11	-0.22	0.37	-0.26	7.25	7.07	(+0.18)	-0.07	7.25	7.26	(-0.01)	-0.19	+0.15
7	Me	7.14	-0.19	0.32	-0.22	7.15	7.11	(+0.04)	-0.06	7.23	7.27	(-0.04)	-0.16	+0.13
8	Et	7.15	-0.18	0.30	-0.21	7.18	7.12	(+0.06)	-0.06	7.26	7.27	(-0.01)	-0.15	+0.12
9	i-Pr	7.15	-0.18	0.30	-0.21	7.22	7.12	(+0.10)	-0.06	7.27	7.27	0.00	-0.15	+0.12
10	t-Bu	7.16	-0.17	0.28	-0.20	7.39	7.13	(+0.26)	-0.06	7.29	7.27	(+0.02)	-0.14	+0.11
11	Ph	7.31	-0.02	0.03	-0.02	7.57	7.31	(+0.26)	-0.01	7.40	7.32	(+0.08)	-0.01	+0.01
12	H	7.33	0	0.00	0.00	7.33	7.33	0.00	0.00	7.33	7.33	0.00	0	0
13	SiMe <sub>3</sub>	7.33	0	0.00	0.00	7.52	7.33	(+0.19)	0.00	7.33	7.33	0.00	0.00	0.00
14	F	7.10	-0.23	0.38	-0.27	7.03	7.06	(-0.03)	-0.08	7.31	7.25	(+0.06)	-0.19	+0.15
15	Cl	7.21	-0.12	0.20	-0.14	7.32	7.19	(+0.13)	-0.04	7.26	7.29	(-0.03)	-0.10	+0.08
16	Br	7.26	-0.07	0.12	-0.08	7.48	7.25	(+0.23)	-0.02	7.20	7.31	(-0.11)	-0.06	+0.05
17	I	7.30	-0.03	0.05	-0.04	7.68	7.29	(+0.39)	-0.01	7.07	7.32	(-0.25)	-0.03	+0.02
18	CO <sub>2</sub> H	7.60	+0.27	0.96	+0.31	8.13	7.64	(+0.49)	+0.14	7.46	7.46	0.00	+0.17	-0.13
19	CO <sub>2</sub> Me	7.53	+0.20	0.71	+0.23	8.04	7.56	(+0.48)	+0.10	7.42	7.43	(-0.01)	+0.13	-0.10
20	CO <sub>2</sub> Et	7.53	+0.20	0.71	+0.23	8.05	7.56	(+0.49)	+0.10	7.42	7.43	(-0.01)	+0.13	-0.10
21	CF <sub>3</sub>	7.53	+0.20	0.71	+0.23	7.61	7.56	(+0.05)	+0.10	7.46	7.43	(+0.03)	+0.13	-0.10
22	Ac	7.55	+0.22	0.79	+0.25	7.95	7.58	(+0.37)	+0.11	7.44	7.44	0.00	+0.14	-0.11

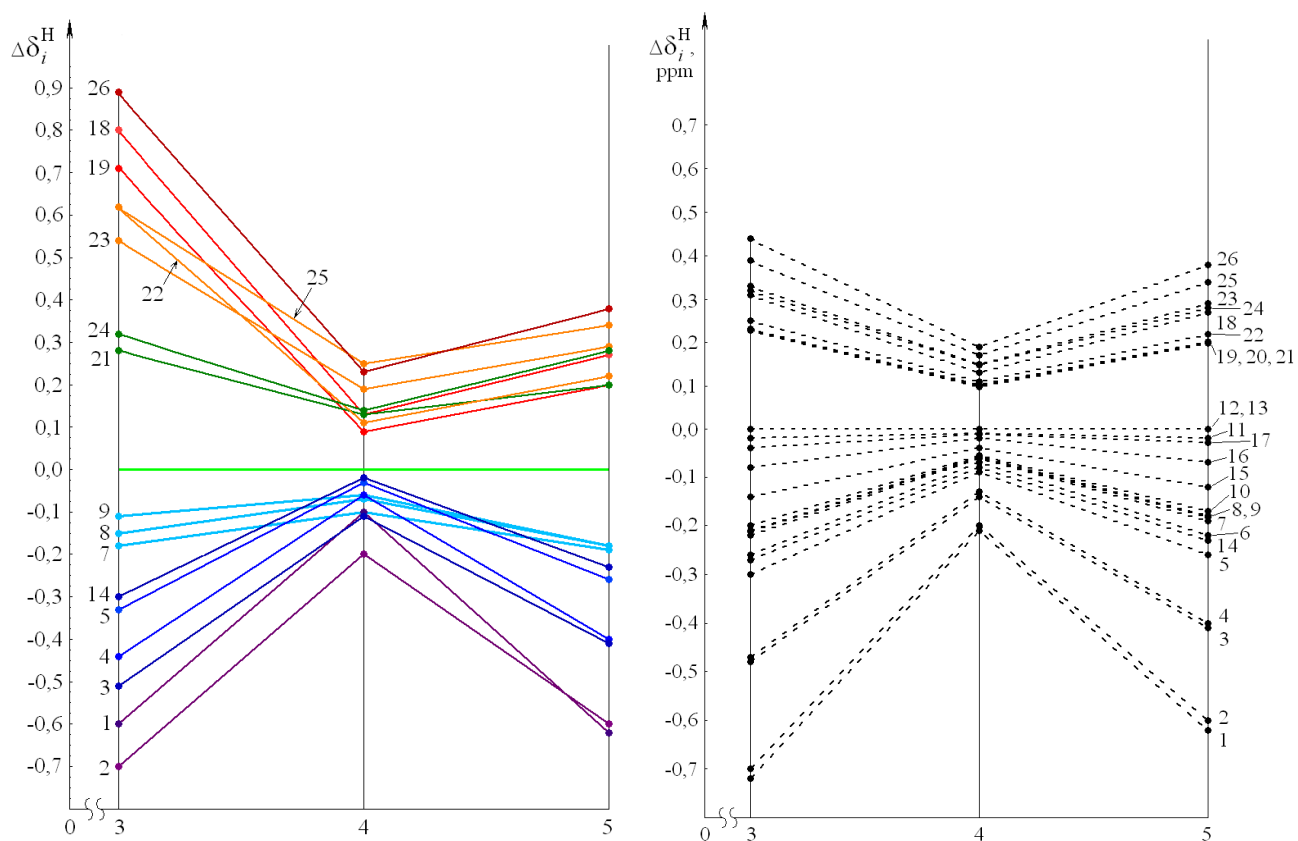
<b>23</b>	CH=O	7.62	+0.29	+1.04	+0.33	7.87	7.66	(+0.21)	+0.15	7.52	7.48	(+0.04)	+0.18	-0.14
<b>24</b>	CN	7.61	+0.28	1.00	+0.32	7.65	7.65	0.00	+0.15	7.47	7.47	0.00	+0.17	-0.14
<b>25</b>	SO <sub>2</sub> Me	7.67	+0.34	+1.21	+0.39	7.95	7.72	(+0.23)	+0.17	7.58	7.50	(+0.08)	+0.22	-0.17
<b>26</b>	NO <sub>2</sub>	7.71	+0.38	1.36	+0.44	8.22	7.77	(+0.45)	+0.19	7.56	7.52	(+0.04)	+0.25	-0.19

### 3.1.3.2. Construction of virtual plots

The real parameters of para-protons  $\delta_o^{H,N}$  represented in Table 1 were taken as points of para-protons (at n=5) for plotting of the right branch of virtual “proportional” plots (Fig. 9). The virtual parameters  $\delta_{m,pr.}^{H,N}$  (Table 2) are used as points of meta-protons (n=4) instead of real ones  $\delta_m^{H,N}$ . These parameters together with virtual parameters  $\delta_{o,pr.}^{H,N}$  (Table 2) were used as points of ortho-protons (n=3) for plotting of the left branch. **The use of just “basic proportional parameters”  $\delta_{o,pr.}^{H,N}$  and  $\delta_{m,pr.}^{H,N}$  ensures the relative “branches parallelism” (branches similarity) in the ideal plots.**

All 26 virtual “ideal” plots are depicted by black dotted lines in right of Fig. 9. For the comparison Fig. 7 is given near (left), where 18 of 26 real plots (see above) are painted indifferent colors. It should be stressed that the real plots by definition **coincide** with ideal ones **only** for the compounds **2** and **24**.

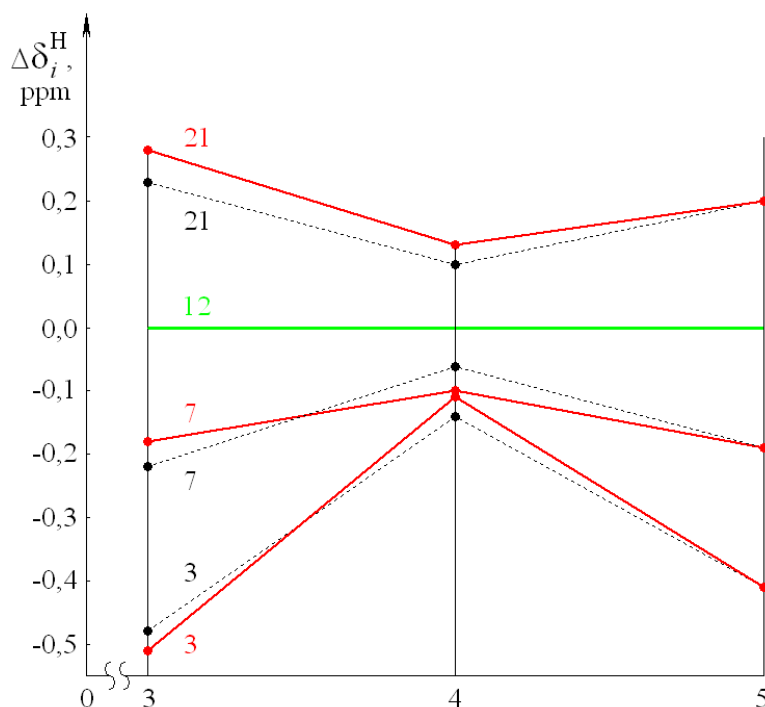
Fig. 9



### 3.1.3.3. The main differences between ideal “proportional” and real plots

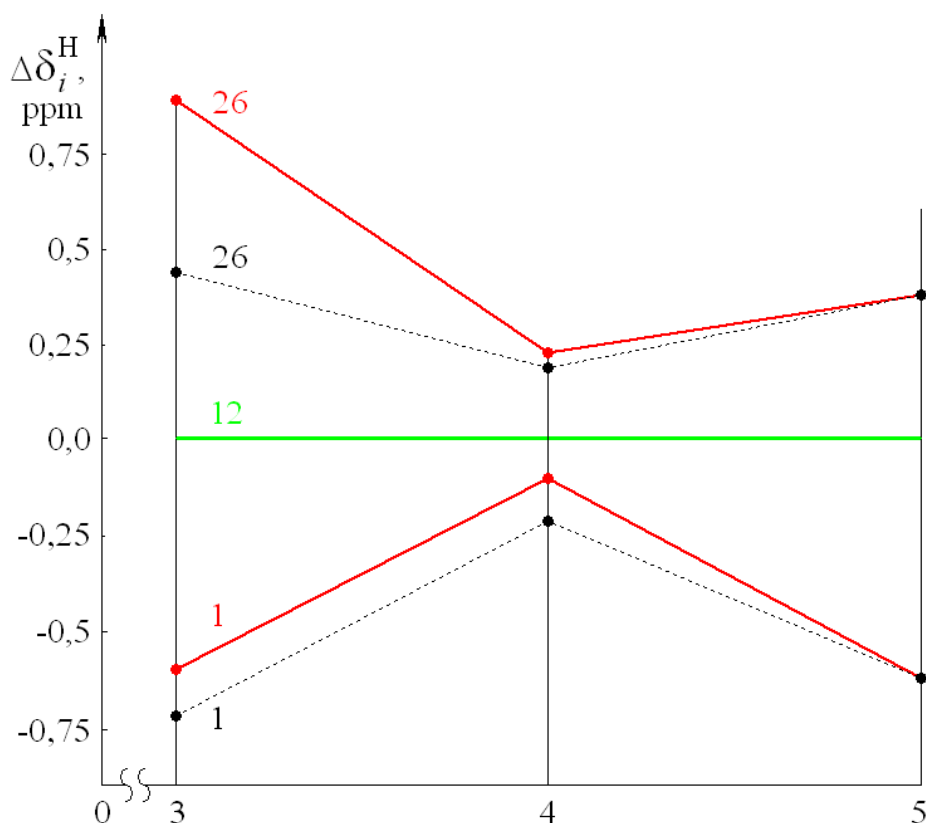
To compare the ideal (black color) and real plots (red color) some fragments of these plots given earlier in Figs. 7 and 8 are represented in Figs. 10 and 11. Fig. 10 represents the most similar parts (plots of the compounds **3**, **7** and **21**), Fig. 11 – the most different parts. We consider that among all plots of 10 compounds with electron-donating substituents (**1**, **3-11**) the real plots of only two compounds (**3** and **7**) are similar to their ideal plots. For the compounds with electron-accepting substituents **18-23**, **25**, **26** the only one plot (for trifluoromethyltoluene **21**) is similar to its ideal shape. The mentioned plots are given in Fig. 10.

Fig. 10



To our mind, the real plots of the compounds **1**, **9**, **18**, **19**, **25** and **26**, as well as compounds **6**, **10**, **11** and **13** (which are not given in Fig. 7) considerably differ from their ideal shape. In Fig. 11 depicted only plots of the compounds **1** and **26**.





### 3.1.3.3.1. Effect of the value of basic ortho-parameters $\delta_o^{H,N}$

The distinction from ideal shape in the real plots is caused by the **shift of ortho-protons absorption** toward **low field**. Due to the shift the difference  $\Delta\Delta\delta_{o,pr}^{H,N}$  between real ( $\delta_o^{H,N}$ ) and “virtual proportional” ( $\delta_{o,pr}^{H,N}$ ) values of the basic spectral parameters (or differential spectral parameters  $\Delta\delta_o^{H,N}$  and  $\Delta\delta_{o,pr}^{H,N}$ , what is the same) increases to  $\Delta\Delta\delta_{o,pr}^{H,N} = + 0.50$  ppm (see Table 2). Such shift toward low field is caused in our opinion by **the increase of substituent Y volume** which has the greatest influence on nearby ortho-protons. Probably we may neglect the “volumetric” effect on the most remote para-protons but the effect on meta-protons is present (see the values of differential parameters  $\Delta\Delta\delta_{m,pr}^{H,N}$  for the compounds **1, 4 and 11** which are close by their absolute values to 0.10 ppm; Table 2).

The confirmation of such assumption validity is the considerable increase of the linear correlation coefficients  $k$  to 0.986 for the dependence of ortho-protons value  $\delta_o^{H,N}$  on Brown’s para-constants during the independent examination of 9 compounds with “volumetric substituents” (**1, 6, 10, 11, 13, 18-20, 26**). The correlation of the second plot constructed of the remaining 9 compounds with less “volumetric” substituents was found to be even better (**2-4, 7-9, 12, 21, 24**) ( $k = 0.998$ ) [3]. If such division is not carried out, the correlation coefficient  $k$  for all 18 compounds is equal to 0.924, as shown in [1].

Let us consider the values of positive parameters  $\Delta\Delta\delta_{o,pr}^{H,N}$  (Table 2) for all monosubstituted benzenes **1-13, 18-26** (except haloid compounds **14-17**). These parameters characterize the shift of ortho-protons absorption toward low field compared with expected shift in the “ideal” plots. The most considerable shifts are observed for the compounds with branched (i.e. non-linear) and “unsaturated” substituents Y, where atom connected with phenyl ring

(branching center) is an element of the periodic system second period (C or N). Thus for nitrobenzene **26** (substituent O-N=O) the parameter  $\Delta\Delta\delta_{o,pr.}^{H,26}$  is equal to +0.45 ppm; for benzoic acid and its esters **18-20** (O=C-OR,  $\Delta\Delta\delta_{o,pr.}^{H,18} = + 0.49$  ppm); for acetophenone **22** (O=C-Me,  $\Delta\Delta\delta_{o,pr.}^{H,22} = + 0.37$  ppm) and for diphenyl **11** (C<sub>6</sub>H<sub>5</sub>,  $\Delta\Delta\delta_{o,pr.}^{H,11} = + 0.26$  ppm). In the less branched (due to the presence of hydrogen atom connected with the branching center instead of oxygen or carbon atom) aldehyde group (O=C-H) in benzaldehyde **23** the parameter  $\Delta\Delta\delta_{o,pr.}^{H,23}$  is already lower (+0.21 ppm).

For the compounds with branched but saturated substituents (NMe<sub>2</sub>, CMe<sub>3</sub>) the value of mentioned shift is within the range of 0.10-0.25 ppm. With the decrease of alkyl group branching degree in the row tert-butylbenzene **10**→cumene **9**→ethylbenzene **8**→toluene **7** the value of the parameter  $\Delta\Delta\delta_{i,pr.}^{H,N}$  decreases: 0.26→0.10→0.06→0.04 ppm.

Let us note the closeness of the parameters  $\Delta\Delta\delta_{o,pr.}^{H,N}$  for dimethylsubstituted compounds: dimethylaniline **1** (NMe<sub>2</sub>,  $\Delta\Delta\delta_{o,pr.}^{H,N} = 0.12$  ppm) and cumene **9** (CHMe<sub>2</sub>,  $\Delta\Delta\delta_{o,pr.}^{H,N} = 0.10$  ppm). These compounds differ only in that the "branching center" in the first case is a nitrogen atom, and the second - a carbon atom. This may indicate that the nature of an atom in the "branching center" does not play a role of the parameter  $\Delta\Delta\delta_{o,pr.}^{H,N}$  value.

For those substituents, atom bonded with phenyl ring of which is an element of the periodic system third period (and it is the branching center - substituents SiRR<sup>1</sup>R<sup>2</sup> or SRR<sup>1</sup>) we also observe the shift of ortho-protons absorption toward low field. For Y = SMe ( $\Delta\Delta\delta_{o,pr.}^{H,6} = 0.18$  ppm), Y = SiMe<sub>3</sub> ( $\Delta\Delta\delta_{o,pr.}^{H,13} = 0.19$  ppm), Y = SO<sub>2</sub>Me ( $\Delta\Delta\delta_{o,pr.}^{H,25} = 0.23$  ppm). It should be noted that the average shift value (about 0.20 ppm) is considerably less than that of the above-mentioned compounds **18-20**, **22-23**, **25-26** with the substituent Y of the general formula CRR<sup>1</sup>R<sup>2</sup> or NRR<sup>1</sup>.

For the compounds **2**, **3-5**, **7**, **12**, **21** and **24** containing linear substituents Y (i.e. non-branched in the point of bonding with phenyl ring) the only small by absolute value ( $\leq 0.05$  ppm) positive and negative parameters  $\Delta\Delta\delta_{o,pr.}^{H,N}$  are observed. Benzonitrile **24** containing "unsaturated" substituent – nitrile group with triple bond C≡N – should be especially noted. To our mind, the main factor stipulating the absence of low-field shift of ortho-protons absorption is the **group linearity**, i.e. the absence of branching in the point of bonding with phenyl ring. Therefore we conclude that **the main factor** that causes the shift of ortho-protons absorption toward low field is a **substituent non-linearity** (its branching) in the point of its bonding with phenyl ring. The presence of unsaturated bonds in this point intensifies this shift.

### 3.1.4. Peculiarities of plots for haloidbenzenes NMR <sup>1</sup>H spectra

Now let us consider in detail the plots of haloidbenzenes **14-17**. It should be stressed that three of four plots are atypical, i.e. they do not belong to the variants represented in Figs. 1 and 2. The exclusion is fluorobenzene **14**, the plot of which corresponds to the variant 1.

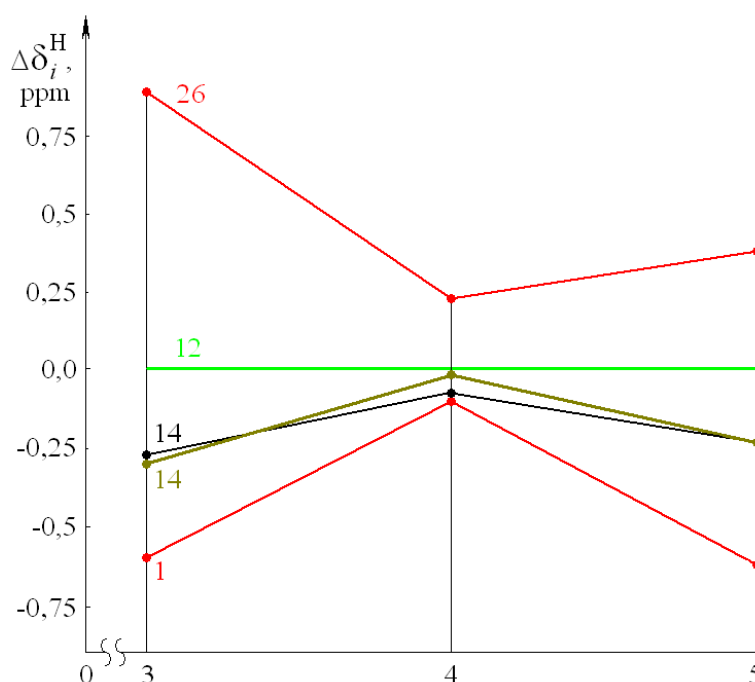
The negative values of differential spectral parameters  $\Delta\delta_p^H$  which are the basis for the construction of "ideal proportional" plots for haloidbenzenes **14-17** indicate on the one hand the

electron-donating character of haloid atoms as substituents and on the other hand – correspond to the expected order of electron-donating properties decrease in the row.

### 3.1.4.1. Fluorobenzene 14

The real (dark green line) and “ideal” (black line) plots of fluorobenzene **14** are represented in Fig. 12, where the real plots of “extreme” compounds **1** and **26** (red lines), as well “intermediate” benzene **12** (light green line) are depicted as reference lines for the comparison.

Fig. 12

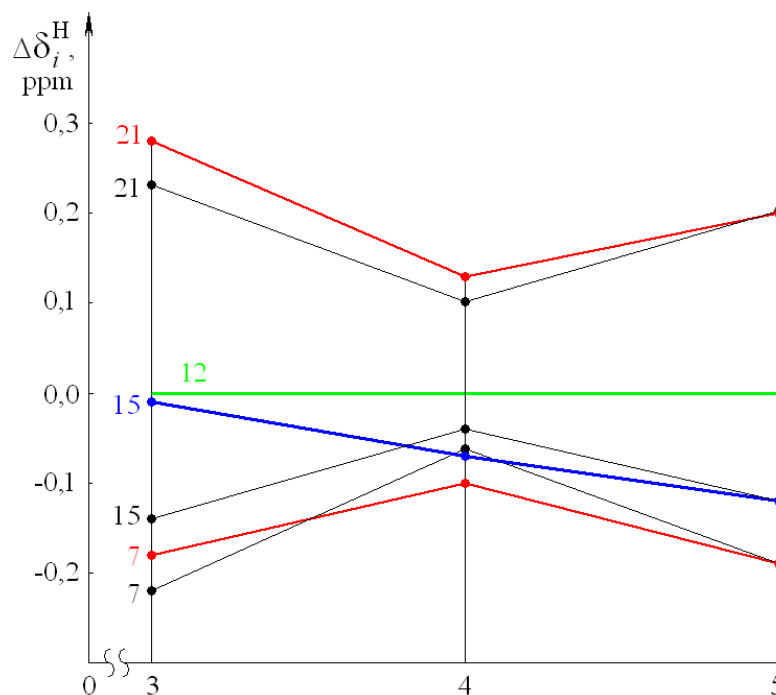


As it was expected, the plot of fluorobenzene **14** is a typical, almost symmetrical (ratio  $|\Delta\delta_{o-p}^{H,14}| / |\Delta\delta_{m-p}^{H,14}| = 0.30 / 0.23 = 1.30$ , sufficiently “high hill” of the **typical compound with electron-donating substituent of the medium strength** ( $k_{14} = -0.23 / -0.60 = 0.43$ ). Its shape may be considered as intermediate one between the shape of “high hill” of aniline **1** and **2** and shape of “low hill” of cumene **9**. To our mind it is closer to the shape of “high hill”. There is some peculiarities in the plot of fluorobenzene **14**: the hill peak (i.e.  $\delta_m^{H,14} = 7.31$  ppm,  $n = 4$ ) is **much closer to the “benzene line”** than it was expected. It is even closer than peak of the “lowest hill” of cumene **9** ( $\delta_m^{H,9} = 7.27$  ppm). The great positive value of the proportional meta-parameter  $\Delta\delta_{m,pr}^{H,14}$  (+ 0.06 ppm) for meta-protons is in a sharp contrast with the negative proportional ortho-parameter  $\Delta\delta_{o,pr}^{H,14} = -0.03$  ppm for ortho-protons. Due to the interaction of mentioned two factors the proportion distortion of fluorobenzene **14** real plot takes place compared with its “ideal proportional” analogue (see Fig. 12).

### 3.1.4.2. Chlorobenzene 15

The plots of chlorobenzene **15** are represented in Fig. 13 as blue line also with reference lines (plots of substances **7**, **12** and **21**). As it was mentioned above, the shape of the real plot is atypical; it corresponds to the variant 3 depicted in Fig. 3. The both branches of the plot are situated in the forth quadrant because the differential parameters  $\Delta\delta_{o-m}^{H,15}$  and  $\Delta\delta_{m-p}^{H,15}$  are the positive values.

Fig. 13



The differential parameter  $\Delta\delta_{o-m}^{H,15} = 7.32 - 7.26 = +0.06$  ppm has a positive sign, whereas the “ideal proportional parameter” has a negative sign ( $\Delta\delta_{o-m,pr}^{H,15} = 7.19 - 7.29 = -0.10$  ppm). The presence of **negative sign** of this parameter means that the left branch should transfer into the first quadrant. The difference between real and ideal parameters is equal to:  $\Delta\delta_{o-m}^{H,15} - \Delta\delta_{o-m,pr}^{H,15} = +0.06 - (-0.10) = +0.16$  ppm. It may be obtained in other way, as a difference between parameters  $\Delta\Delta\delta_{o,pr}^{H,15} - \Delta\Delta\delta_{m,pr}^{H,15}$ :  $+0.13 - (-0.03) = +0.16$  ppm. It means that the presence of left branch in the forth (not in the first) quadrant is determined by a great positive value of the parameter  $\Delta\Delta\delta_{o,pr}^{H,15}$  (+0.13 ppm) on the one hand and a small negative value of the parameter  $\Delta\Delta\delta_{m,pr}^{H,15}$  (-0.03 ppm) on the other hand. Thus, the deviation from “ideal” plot of “low hill” (see black line in Fig. 13) expected for the para-protons parameter ( $\delta_p^{H,15} = 7.21$  ppm) is determined by the simultaneous action of two factors: 1) the increase of  $\Delta\Delta\delta_{o,pr}^{H,15}$  parameter and 2) the decrease of  $\Delta\Delta\delta_{m,pr}^{H,15}$  parameter. Both factors cause the “hill flattening” and even “hill reversing”. Obviously, the great by absolute value and positive by sign parameter  $\Delta\Delta\delta_{o,pr}^{H,15}$  plays the main role in “flattening-reversing” of the plot left branch and results in its transition into the forth quadrant.

Let us examine here the plots of other two compounds (tert-butylbenzene **10** and diphenyl **11**) which correspond to the third variant (Fig. 3), the same as chlorobenzene **15** plot. The both

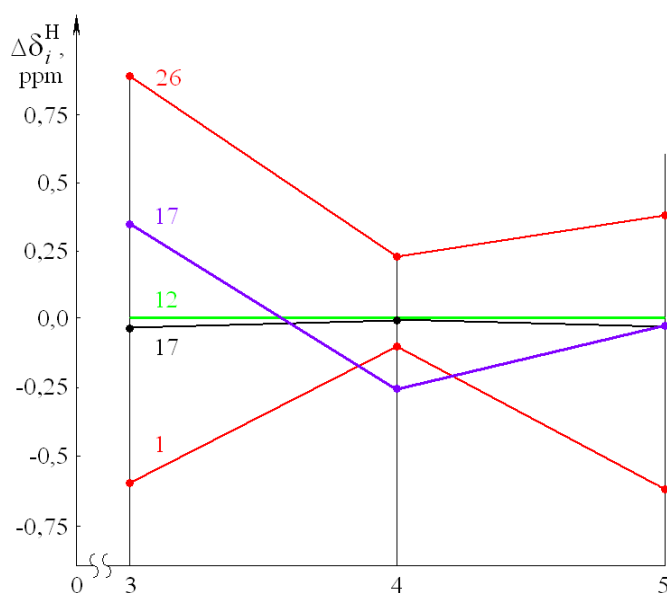
compounds contain weak substituents Y relative to electron-donating strength (coefficients  $k_N$  in Table 2 are equal to 0.28 and 0.03, respectively). Therefore their negative proportional ortho-parameters  $\Delta\delta_{o,pr.}^{H,N}$  have small absolute values ( $\Delta\delta_{o,pr.}^{H,10} = -0.20$  ppm, and  $\Delta\delta_{o,pr.}^{H,11} = -0.02$  ppm) and “ideal proportional” plots represent “low hill” for tert-butylbenzene **10** and “almost flat hill” for diphenyl **11** (Fig. 8).

On the other hand, as it was mentioned above, both groups are strongly **branched in the point of bonding with phenyl ring**. Their parameters  $\Delta\Delta\delta_{o,pr.}^{H,N}$  have great values and equal to +0.26 ppm. Therefore during the transition from the ideal plots (where **parameter  $\Delta\delta_{o,pr.}^{H,N}$**  is used to plot the left branch) to the real ones (where **parameter  $\Delta\delta_o^{H,N}$**  is also used to plot the left branch) the value of the differential parameter  $\Delta\Delta\delta_{o,pr.}^{H,N}$  equal to their difference is of great importance. If the parameter  **$\Delta\Delta\delta_{o,pr.}^{H,N}$  is greater** than the absolute value of the proportional parameter  **$\Delta\delta_{o,pr.}^{H,N}$** , the **left branch transits from the first to the forth quadrant**, i.e. variant 3 is realized. Just this case takes place in the examined examples for tert-butylbenzene **10** and especially for diphenyl **11**. If the mentioned parameters are equal, i.e.  $\Delta\Delta\delta_{o,pr.}^{H,N} = |\Delta\delta_{o,pr.}^{H,N}|$ , the left branch is parallel to the abscissa, the same as for thioanisole **6**, the real plot of which is represented in Fig. 4 (variant 4) as an individual case.

### 3.1.4.3. Bromobenzene 16

The real (light purple line) and ideal (black line) plots of bromobenzene **16** are represented in Fig. 14 with reference lines for the comparison.

Fig. 14



As it was mentioned above, the shape of the real plot (corresponds to “pit” obtained by variant 2 (Fig. 2). However in contrast to other “pits” typical of described above compounds **18-26** the bottom point of bromobenzene “pit” ( $\delta_m^{H,16} = 7.20$  ppm) is under the “benzene line” ( $\delta_i^{H,12} = 7.33$  ppm). At the same time the “ideal proportional plot” calculated for the value of para-protons absorption in bromobenzene **16** ( $\delta_p^{H,16} = 7.26$  ppm,  $\Delta\delta_p^{H,16} = -0.07$ ) is expected to be as “very low

**hill**" (see black line in Fig. 14) which is even lower than "low hill" of chlorobenzene **15** (cf. black line in Fig. 13).

Such dramatic change of the plot shape (its reversing followed by lengthening) is caused by **simultaneous transition of every branch into the quadrant opposite to the expected one**. The transition of the left branch into the fourth quadrant (instead of expected first quadrant) is the same as the transition of chlorobenzene **15**, i.e. it is stipulated by: 1) considerable value of positive parameter  $\Delta\Delta\delta_{o,pr.}^{H,16}$  (+ 0.23 ppm, cf.  $\Delta\Delta\delta_{o,pr.}^{H,15} = + 0.16$  ppm) and 2) considerable value of negative parameter  $\Delta\Delta\delta_{m,pr.}^{H,16}$  (- 0.11 ppm, cf.  $\Delta\Delta\delta_{m,pr.}^{H,15} = - 0.03$  ppm). Due to the increase of absolute values of both parameters  $\Delta\Delta\delta_{i,pr.}^{H,16}$  (in comparison with the analogous parameters of chlorobenzene **15**) the left branch of bromobenzene **16** real plot is more abrupt ( $|\Delta\delta_{o-m}^{H,16}| = 0.28$  ppm) than that of chlorobenzene **15** ( $|\Delta\delta_{o-m}^{H,15}| = 0.06$  ppm).

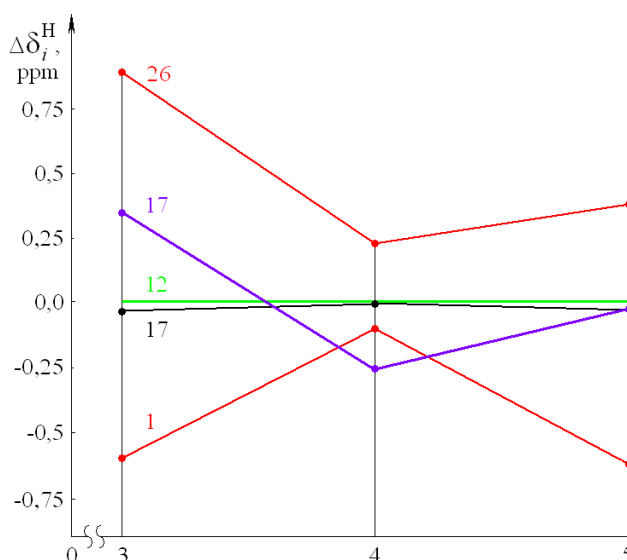
In contrast to the right branch of chlorobenzene **15** real plot preserving the expected location in the fourth quadrant, **the right branch of bromobenzene 16 real plot "turns inside out"** and transits into the **first quadrant**. Such transition is stipulated by the great value of negative parameter  $\Delta\Delta\delta_{m,pr.}^{H,16}$  (- 0.11 ppm). The result (at constant value of the basic parameter  $\delta_p^{H,16} = \delta_{p,pr.}^{H,16} = 7.26$  ppm) is sign change of the parameter  $\Delta\delta_{m-p}^{H,16}$  defining the location of right branch, for negative one ( $\Delta\delta_{m-p}^{H,N} = 7.20 - 7.26 = - 0.06$  ppm). The same as for the left branch, in the "ideal proportional plot" the right branch is determined by the value  $\Delta\delta_{m-p,pr.}^{H,16} = 7.31 - 7.26 = + 0.05$  ppm, what supposes its location in the fourth quadrant.

As a result, the transition of every branch of bromobenzene **16** real plot into the opposite quadrant is observed. The expected "very low hill" transforms into "deep pit" (due to the increase of both branches steepness) and "pit bottom pierces the benzene line". It should be noted that the left branch is more abrupt than the right one.

#### 3.1.4.4. Iodobenzene 17

The real (purple line) and ideal (black line) plots of iodobenzene **17** are represented in Fig. 15 with reference lines for the comparison.

Fig. 15



Its shape corresponds to the deeper “pit” compared with that of bromobenzene (Fig. 14). All aforesaid concerning the reasons of “almost flat hill” transformation into “very deep pit” (with the increase of both branches steepness) for bromobenzene **16** pertains to iodobenzene **17** in a greater degree. Thus, the parameter  $\Delta\Delta\delta_{o,pr}^{H,17} = + 0.39$  ppm is greater by order than the absolute value of proportional parameter  $|\Delta\delta_{o,pr}^{H,17}| = 0.04$  ppm and the parameter  $\Delta\Delta\delta_{m,pr}^{H,17} = - 0.25$  ppm is greater by its absolute value than the parameter  $\Delta\delta_{m,pr}^{H,17} = 7.32 - 7.30 = + 0.02$  ppm defining the location of the right branch of “ideal proportional plot” in the forth quadrant.

All mentioned above explain the transition of every branch of iodobenzene **17** real plot into the opposite quadrant and the transformation into “very deep pit” which pierces not only “benzene line” but the line of minimum parameter  $\Delta\delta_{m,min}^{H,N}$  as well. The latter line is determined by the second minimum parameter  $\Delta\delta_m^{H,2} = - 0.20$  ppm pertinent to aniline **2**. Let us note the increase of both branches steepness ( $|\Delta\delta_{o-m}^{H,17}| = 0.60$  ppm and  $|\Delta\delta_{m-p}^{H,17}| = 0.23$  ppm) even compared with “pit” of bromobenzene **16**. The same as for bromobenzene **16**, the left branch of iodobenzene **17** plot is more abrupt than its right one.

### 3.1.5. Discussion of anomalies of haloidbenzenes 14-17 real plots

In the row of haloidbenzenes the difference **between expected and experimental values** of ortho-parameters  $\delta_o^{H,N}$  **sharply increases with the increase** of haloid periodic number. For two latter members of the row (**bromobenzene, iodobenzene**) the experimental values  $\delta_o^{H,N}$  considerably exceed the values of benzene parameter  $\delta^{H,12}$ . Therefore, they pass into the area of parameters typical of **electron-accepting substituents of medium strength instead of expected** parameters typical of weak **electron-donating substituents**.

Such stepwise increase of haloids atom radiuses in the row of **14→15→16→17** causes the **rising effect of volumetric haloid substotuent Y** on the ortho-protons closely located in the space. As a result, the basic spectral parameter  $\delta_o^{H,N}$  shifts toward the low field and both differential spectral parameters ( $\Delta\delta_{o-m}^{H,N}$ ,  $\Delta\Delta\delta_{o,pr}^{H,N}$ ) increase. Finally the plot left branch transits from the first into the forth quadrant already for chlorobenzene **15**.

At the same time we observe in the row the unexpected and unexplained parallel shift of the basic parameter  $\delta_m^{H,N}$  toward the high field and increase of the negative values of differential spectral parameters ( $\Delta\delta_{m-p}^{H,N}$  and  $\Delta\Delta\delta_{m,pr}^{H,N}$ ). Finally the plot right branch transits from the first into the forth quadrant (compounds **16 and 17**). We **have not explanation** of the observed shift of meta-protons absorption toward the high field in the row **14→15→16→17**, therefore we only establish the fact<sup>4</sup>.

Unlike the parameters  $\delta_o^{H,N}$  and  $\delta_p^{H,N}$  (**N = 14–17**), the course of **experimental parameters**  $\delta_m^{H,N}$  for meta-protons in the haloidbenzenes row is almost opposite to that of the **calculated** proportional parameters  $\delta_{m,pr}^{H,N}$ . Let us note that this “reverse” motion starts from unexpected

<sup>4</sup> Generally, some other changes of differential meta-parameters  $\Delta\Delta\delta_{m,pr}^{H,N}$  (Table 2) are incomprehensible. In particular, it is the greatest increase (except haloidbenzenes) of mentioned parameter by its absolute value (by 0.10 ppm) during the transition from aniline **2** to dimethylaniline **1**. We could not find any regular dependence between parameter values and substituent structure.

“direct motion” described for the fluorine atom above and then turns to the opposite side with unprecedented value of the every pace.

Thus we observe the gradual transformation of “high hill” typical of the compounds with **electron-donating substituents** of fluorobenzene **14** into the “pits” typical of the compounds with **electron-accepting substituents** of bromobenzene **16** and especially of iodobenzene **17**. Moreover, these “pits pierce the benzene line” what is not observed for the typical compounds with electron-acceptor substituents **18-26**. It should be noted that such contradiction is caused by non-uniform directional motion of basic parameters  $\delta_i^{H,N}$  ( $i = o-, m-$ ) in the row of haloidbenzenes **14-17**.

To conclude we note that fluorine is the most typical substituent Y among 4 haloid atoms, because the spectral behavior of fluorobenzene **14** does not go beyond the expected behavior of the compounds with electron-donating substituents. On the contrary, the “spectral” behavior of haloidbenzenes **15-17 deviates from the expected behavior more and more** with the increase of the haloid atom number in the periodic system.

### **3.2. Para-protons**

Let us discuss now the ratio between the basic and differential spectral parameters of para-protons  $\delta_p^{H,N}$  and  $\Delta\delta_p^{H,N}$  in the row of haloidbenzenes **14-17** and compare them with the same values of other monosubstituted benzenes (**1-11 and 18-26**). We use the generally accepted parameters characterizing the influence of the substituent Y in monosubstituted benzenes **1-26** on the various physical and chemical properties of the mentioned compounds.

We ascertained [1, 2] that the chemical shifts of para-protons ( $\delta_p^{H,N}$ ) in monosubstituted benzenes **1-26** are in a good agreement with the parameters of Hammett types constants ( $\sigma_p$ ), especially with Brown’s constants ( $\sigma_p^+$ ). It is well-known that last these constants are the best for the reactions, where the substituent is capable to conjugate with the reaction center. As it was shown above, the spectral para-parameters  $\delta_p^{H,N}$  and  $\Delta\delta_p^{H,N}$  of haloidbenzenes uniquely indicates the **electron-donating** character of all four haloid atoms as the substituents.

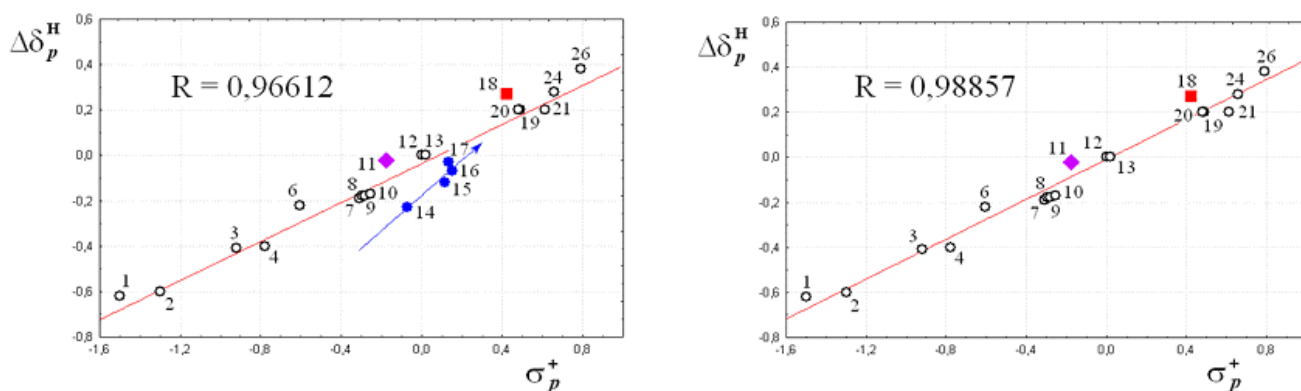
#### **3.2.1. Discussion of anomalies in haloidbenzenes 14-17 para-type constants ( $\sigma_p$ ) – as parameters characterizing the substituent Y**

It was shown in [2] that haloid atoms as the substituents Y in the row of monosubstituted benzenes **1-26** almost always worsen the correlation of the various dependencies of  $\Delta\delta_p^{H,N}$ -  $\sigma_p$  type. The points of haloids on corresponding plots are located at a distance (sometimes very far) from plotted straight line of maximum correlation.

The plot of dependence  $\Delta\delta_p^{H,N}$ -  $\sigma_p^+$  with the highest correlation coefficient among all examined plots in [1] is represented on the left site of Fig. 16. The point of fluorobenzene **14** is located at the largest distance; the points of chlorobenzene **15** and bromobenzene **16** are located considerably nearer and the point of iodobenzene **17** does not worsen the correlation. If we eliminate 4 points of haloid benzenes (considering the haloid atoms as a separate group of



substituents), the essential increase of R value to 0.989 takes place for the remaining 18 compounds. This plot is shown in the right-hand side of the Fig. 16



There is direct evidence of paradox: on the plot  $\Delta\delta_p^{H,N}$  vs  $\sigma_p^+$  the **best** (relatively to the expected “spectral behavior”) **fluorobenzene 14** (see above), containing the strongest electron-donating substituent among four halogens – fluorine - **worsens the correlation most of all**. And vice versa, the **worst** iodobenzene **17** practically does not influence the correlation. To examine this paradox, let us analyze the ratio between different types of haloid substituent constants.

### 3.2.2. Comparison of different constants of haloid substituents Y (F, Cl, Br and I)

To determine the presence (or absence) of the linear dependencies of  $\delta_i^{H,N}$ –  $\sigma$  type in monosubstituted benzenes **1-26** [1] we chose the most widespread, to our mind, sets of constants obtained during the investigations of different chemical reactions of aromatic compounds. The halogen atoms constants as the substituents are included in the majority of sets.

#### 3.2.2.1. Reasons of choice of investigated sets of substituent constants

It is well-known that the constants of the same substituent (e.g. Cl) may considerably differ depending upon the reaction type for which the constant set is obtained. For example, the value of Brown’s para-constant set for chlorine atom ( $\sigma_{p,Cl}^+ = + 0.11$ ) is considerably less than that of Hammett’s para-constant set ( $\sigma_{p,Cl} = + 0.23$ ), and set of Yukawa-Tsuno resonance constants for chlorine has at all the negative value (Yukawa-Tsuno constants set  $\Delta\sigma_{R,Cl}^+ = - 0.167$ , and resonance constant  $\sigma_{R,15}^+ = - 0.19$ ).

Moreover, the constant value of the same substituent (e.g. fluorine) may vary even inside the same set of constants (e.g. set of Hammett’s para-constants  $\sigma_{p,F}$ ). Depending on the information source, the value may differ by 0.1: in [4] the value  $\sigma_{p,F}$  is equal to + 0.06 and in [5]  $\sigma_{p,F} = + 0.15$ . In such a case we need to select one value which we’ll use further.

The constants from 4 sets for every haloid atoms are represented in Table 3. For the mentioned constants the best correlations of the linear dependencies  $\delta_i^{H,N}$ –  $\sigma$  were found in [1]. The sets are: 1) Hammett’s para-constants  $\sigma_p$ ; 2) Brown’s para-constants  $\sigma_p^+$ ; 3) Yukawa-Tsuno resonance constants  $\Delta\sigma_{R,N}^+$ ; 4)  $\sigma_{R,N}^+$  and  $\sigma_{R,N}^-$  resonance constants. In [1] we chose the most

reliable (to our mind) constants and they are represented in Table 3 with the accuracy of 0.01. Moreover the same constants for some subsidiary components with electron-donating (**2**, **4**, **7**) and electron-accepting (**18**, **19**, **21**, **24**, **26**) substituents are also represented there for the comparison. "Spectral" Brown's para-constants suggested by us (see below) are also given in Table 3.

Table 3

**Constants of the substituents Y in monosubstituted benzenes taken from [1]**

No	Substituent Y	Dimensionless values of constants				
		Hammett $\sigma_p$	Brown		Resonance	
			$\sigma_p^+$	$\sigma_{p,sp}^+$	Yukawa-Tsuno $\Delta\sigma_{R,N}^+$	$\sigma_{R,N}^+ \text{ or } \sigma_{R,N}^-$
<b>14</b>	F	+0.06	-0.07	-0.55 (-0.54)	-0.29	-0.26
<b>15</b>	Cl	+0.23	+0.11	-0.3 (-0.29)	-0.17	-0.19
<b>16</b>	Br	+0.23	+0.15	-0.2 (-0.18)	-0.15	-0.16
<b>17</b>	I	+0.18	+0.14	-0.1(-0.09)	-	-0.18
<b>2</b>	NH <sub>2</sub>	-0.66	-1.30	-1.35 (-1.37)	-1.00	-1.23
<b>3</b>	OH	-0.37	-0.92	-0.9 (-0.93)	-0.68	-0.71
<b>7</b>	CH <sub>3</sub>	-0.17	-0.31	-0.4 (-0.43)	-0.19	-0.22
<b>18</b>	COOH	+0.45	+0.42	+0.6 (+0.61)	-	-
<b>19</b>	COOCH <sub>3</sub>	+0.45	+0.49	+0.45 (+0.45)	-	+0.28
<b>21</b>	CF <sub>3</sub>	+0.54	+0.61	+0.45 (+0.45)	-	-
<b>24</b>	CN	+0.66	+0.66	+0.6 (+0.63)	-	+0.29
<b>26</b>	NO <sub>2</sub>	+0.78	+0.79	+0.85 (+0.86)	-	+0.45

### 3.2.2.2. Comparison of subsidiary components constants from different sets

The constants of subsidiary components with the most electron-donating substituents **1-6** (represented in Table 3 as aniline **2** and anisole **4**) have the greatest negative value. Such values of the parameters are explained by the fact that the substituent atom bound with phenyl nucleus (nitrogen or oxygen) has one (nitrogen) or two (oxygen) free electron pairs capable of conjugation with aromatic fragment. Brown's constants have maximum absolute values and Hammett's constants are about half of them. The values of resonance constants are between them but closer to Brown's constants, especially for  $\sigma_{R,N}^+$  constants. The same situation is observed for the constants of toluene **7** (and other alkylbenzenes **8-10** not represented in Table 3). Their negative values are several times less than those of the compounds **1-6**. The explanation is the absence of free electron pairs capable of conjugation with phenol ring in the alkylbenzenes **7-10**.

For subsidiary compounds with electron-accepting substituents Y (**18-26**) there is another ratio between positive values of discussed constants. Hammett's constants are equal to Brown's constants and twice as much compared with resonance constants. It should be also noted that maximum positive values of Brown's constants ( $\sigma_{p,NO_2} = \approx \sigma_{p,NO_2}^+ = + 0.79$ ) are about half of maximum absolute values of Brown's constants for the compounds with electron-donating substituents ( $\sigma_{p,NMe_2}^+ = - 1.5$ ). While comparing all 4 sets of constants we conclude that the **set of "experimental" Brown's para-constants  $\sigma_p^+$**  unites both types of substituents (electron-donating and electron-accepting) in phenyl ring in the best way.

### **3.2.2.3. Discussion of constants of haloid substituent and subsidiary compounds taken from different sets**

Now let us examine the data for halidbenzenes **14-17**. One can see from Table 3 that **for every halogen atom their positive values** decrease by 0.1 while transition from Hammett's constants to Brown's constants. Then while transition to the resonance constants the values decrease by 0.2-0.3 and the constant sign changes for negative one.

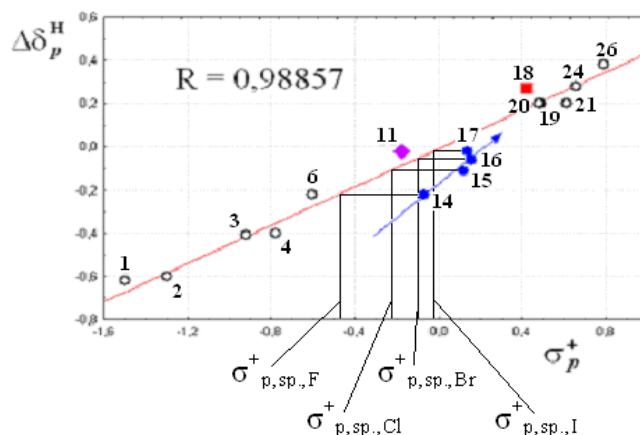
It is considered that both sets of **resonance constants** maximally take into account the resonance interaction between the substituent and reaction center. Therefore we may suppose that **Brown's para-constants for the derivatives of phenol and aniline 1-5** will be **equal** to the **resonance constants** of mentioned compounds (see Table 3) and also **will maximally take into account the resonance interaction** between the substituent and reaction center.

As it was repeatedly stressed, the differential para-parameters of haloidbenzenes  $\Delta\delta_p^{H,N}$  (N = **14-17**) **have negative** values. There is a definite parallelism concerning the change of  **$\Delta\delta_p^{H,N}$  parameters** on the one hand and **resonance constants  $\Delta\sigma_{R,N}^+$  and  $\sigma_{R,N}^+$**  – on the other: a) for fluorine  $\Delta\delta_p^{H,F} = - 0,23$  and  $\Delta\sigma_{R,F}^+ = - 0.29$  and ( $\sigma_{R,F}^+ = - 0.26$ ); for chlorine – 0.12 and –0.17 (– 0.19), respectively; for bromine – 0.07 and – 0.15 (– 0.16), respectively; for iodine – 0.03 and (– 0.18), respectively. It is logical to assume that **chemical shifts of para-protons** (described by  $\Delta\delta_p^{H,N}$  parameters) **correlate with resonance interaction of haloid atoms** (as the substituent) and **reaction center** what is para-proton in our case.

### **3.2.3. Introduction of idea about hypothetical "spectral" Brown's para-constants $\sigma_{p,sp,N}^+$**

Let us calculate the virtual values of Brown's para-constants for the hypothetical case (Fig. 17), when all points of haloidbenzenes **14-17** are on the straight line plotted for 18 remaining compounds and called as "main" line (see the right-hand side of the Fig. 16 ). The following parameters are used for this straight line equation ( $Y=A+BX$ ):  $A = -0.0085$ ;  $B = 0.44324$ . Then the values of **hypothetic "spectral" Brown's para-constants** (denoted as  $\sigma_{p,sp,N}^+$ ) may be calculated in accordance with the formula:  $X = \sigma_{p,sp,N}^+ = (Y + 0.0085)/0.44324$ . The following spectral Brown's

parameters are given in Table 3 with the accuracy of 0.05<sup>5</sup>:  $\sigma_{p,sp,F}^+ = -0.55$ ;  $\sigma_{p,sp,Cl}^+ = -0.3$ ;  $\sigma_{p,sp,Br}^+ = -0.2$ ;  $\sigma_{p,sp,I}^+ = -0.1$ . “Spectral” Brown’s constants  $\sigma_{p,sp,N}^+$  may be also determined graphically with acceptable accuracy. It is necessary to move each of 4 points of haloid atoms located on the second (blue) line to the left and parallel to the abscissa till intersection with plot main (red) line. Then it is necessary to drop perpendicular from this point on the abscissa (Fig. 17) and determine the obtained segments as “spectral” Braun’s para-constants  $\sigma_{p,sp,N}^+$ .



In the same way the values  $\sigma_{p,sp,N}^+$  for subsidiary components were calculated. They are represented in Table 3. All “spectral” Brown’s para-constants  $\sigma_{p,sp,N}^+$  (for both electron-donating and electron-accepting substituents) differ by less than 0.1 from the analogous constants of Brown’s para-set  $\sigma_p^+$ , except values for carboxyl (in **18**), phenyl (in **11**) and trifluoromethyl (in **21**) groups.

As we’ll show in the following papers, “spectral” Brown’s para-constants  $\sigma_{p,sp,N}^+$  (including those of haloidbenzenes) may be also calculated from NMR <sup>13</sup>C spectra of the same monosubstituted benzenes **1-26**, as well as from NMR <sup>9</sup>F spectra of para-fluorobenzenes p-F-C<sub>6</sub>H<sub>4</sub>-Y.

### 3.2.3.1. Comparison of “spectral” Brown’s para-constants and analogous constants from other sets

Comparing the values of “spectral” Brown’s para-constants  $\sigma_{p,sp,N}^+$  for the row of haloidbenzenes **14-17** with other para-constants given in Table 3, the interesting conclusions may be done.

For the fluorine atom the negative “spectral” constant  $\sigma_{p,sp,F}^+$  is twice as large by absolute value compared with negative resonance constants  $\Delta\sigma_{R,F}^+$  and  $\sigma_{R,F}^+$  (0.55 vs 0.26 or 0.29). At the same time for phenols and anilines the negative values of  $\sigma_{p,sp,N}^+$  on the one hand, and  $\Delta\sigma_{R,N}^+$  and  $\sigma_{R,N}^+$  on the other hand are **approximately equal** (e.g.,  $\sigma_{p,sp,NH_2}^+ = -1.35$ , and  $\sigma_{R,NH_2}^+ = -1.23$ ). Therefore we may suppose that **resonance constants of the fluorine atom** ( $\Delta\sigma_{R,F}^+$  and  $\sigma_{R,F}^+$ )

<sup>5</sup> In Table 3 in brackets there are values of “spectral Brown’s constants calculated with the accuracy of 0.01. It seems that owing to the great sensitivity of the “main” line slope (Fig. 16) to even slight change of  $\Delta\delta_p^{H,N}$  parameters (e.g. while rounding the value given with the accuracy of 0.001 to the value with the accuracy of 0.01; not to mention different values obtained from different literature sources) there is no sense to tend to the accuracy higher than 0.05.

incompletely take into account the maximum capability of conjugation. The “spectral” constant  $\sigma_{p,sp.,N}^+$  in particular may be a criterion of this effect for every substituents Y.

The less differences between  $\sigma_{p,sp.,N}^+$  negative values and resonance constants  $\Delta\sigma_{R,F}^+$  and  $\sigma_{R,F}^+$  are observed for the chlorine atom (0.30 vs 0.17 or 0.19). For the bromine atom they are practically the same (0.20 vs 0.15 or 0.16). This equality may be interpreted in such a way that resonance constants of brombenzene completely reproduce the capability of bromine atom conjugation with hydrogen para-atom. The opposite situation is for iodine atom. The absolute value of resonance constant  $\sigma_{R,17}^+$  exceeds the “spectral” one (0.18 vs 0.10). Therefore we may suppose that **resonance constant  $\sigma_{R,17}^+$**  even overrates the iodine atom capability of conjugation with reaction center.

At the same time the difference between “experimental” ( $\sigma_{p,Hal}^+$ ) and “spectral” ( $\sigma_{p,sp.,Hal}^+$ ) Brown’s para-constants for haloids is huge: from +0.25 to +0.5. Thus, for fluorine the difference is:  $-0.07 - (-0.55) = +0.48$ ; for chlorine:  $+0.11 - (-0.30) = +0.41$ ; for bromine:  $+0.15 - (-0.20) = +0.35$ ; for iodine:  $+0.14 - (-0.10) = +0.24$ . For other substituents (except COOH, Ph и CF<sub>3</sub>) this difference is considerably less and does not exceed  $\pm 0.10$ .

There is another interesting observation. Let us compare the values of negative “spectral” Brown’s para-constants  $\sigma_{p,sp.,N}^+$  for the substituents, where the atom of the second period (N, O, F) is bound with phenyl ring. As a number of unshared electron pairs near the atom bound with phenyl ring from aniline **2** (atom - nitrogen, 1 electron pair,  $\sigma_{p,sp.,NH_2}^+ = -1.3$ ), via phenol **3** (oxygen, 2 electron pairs,  $\sigma_{p,sp.,OH}^+ = -0.9$ ) to fluorobenzene **14** (fluorine, 3 electron pairs,  $\sigma_{p,sp.,F}^+ = -0.5$ ) increases, **the absolute value** of “spectral” Braun’s para-constant  $\sigma_{p,sp.,N}^+$  **decreases by 0.4** for every pace, i.e. for every additional free electron pair. This decrease is symbate with the decrease of absolute value of para-protons parameter ( $\Delta\delta_p^{H,N}$ ) by the value equal to 0.19 ppm ( $-0.60 \rightarrow -0.41 \rightarrow -0.23$ ).

The analogous but greater by value change of the chemical shift is also observed for the aliphatic compounds. Thus, in the row of monosubstituted alkyls (e.g. methyls of the general formula Me-Y) with the same substituents the transition from methylamine (Y=NH<sub>2</sub>) via methanol (Y=OH) to methylfluoride (Y=F) is accompanied by the shift toward the low field of methyl group protons absorption by 1.0 ppm ( $2.3 \rightarrow 3.3 \rightarrow 4.3$  ppm).

### **3.3. Final part**

To conclude it should be noted that the behavior of haloid atoms as substituents in haloidbenzenes remains still incomprehensible. There are a lot questions without answers.

Firstly, what is the reason of anomalous spectral behavior of ortho- and meta-protons in haloidbenzenes discussed above?

Secondly, why for the different types of reactions the difference in constants characterizing the substituent (e.g. difference between Hammett’s and Brown’s constants) is greater for haloid atoms than those for other substituents?

And thirdly, why in the set of “experimental” Brown’s para-constants the haloidbenzenes constants  $\sigma_{p, \text{Hal}}^+$  (chlorine and especially fluorine) incompletely characterize the maximum capability of conjugation with aromatic ring in contrast to the constants of other substituents **1-13** and **18-26**?

Let us consider some philosophic thoughts about the inconsistency of physical and chemical properties of haloids as elements of the main sub-group, seventh group of the periodic system.

On the one hand, fluorine, as it was expected, is the most active and reactive oxidant. On the other hand, atomic bonding C-F was found to be unexpectedly strong and insufficiently reactive, consequently teflon, for instance, became a classic compound used for different types of insulation.

Further. On the one hand, fluorine electronegativity ( $\approx 4.0$ ) has the expected maximum value among all elements, including haloids. On the other hand, hydrofluoric acid was found to be the weakest among all hydrohaloid acids. On the contrary, hydroiodic acid is the strongest acid though iodine electronegativity is minimal ( $\approx 2.5$ ). Moreover, the fluorides of light alkaline metals (Li, Na) are badly dissolved in water, whereas the analogous salts of other haloids, iodine in particular, are dissolved very well.

Therefore we may understand the dictum stated by K.Ingold: «The quantitative understanding of the chemical effects of halogen substituents has long provided a difficult hurdle for organic chemistry».

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