# The effect of branching in alkyl substituents on the value of chemical shifts of nuclei of H-2 and H-3 atoms of phenyl ring in NMR ^{1}H spectra of monosubstituted para-alkylaromatic compounds.

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Abstract. The analysis of aromatic proton's chemical shifts in ^{1}H NMR spectra of **21 series of** disubstituted para-alkylaromatic compounds of the general formula $p$-Y-$C_6H_4$-$(CH_2)_r$-$CR^1R^2R^3$ (where r=0 or r=1) was made. It is shown that (as in the case of monoalkylbenzenes, unsubstituted and substituted in the alkyl chain) increase the number of methyl groups at α-carbon atom leads to a downfield shift absorption of ortho- and meta-protons (positive α-effect), and with the introduction of methyl groups to the β-carbon atom is observed negative β-effect – upfield shift of the ortho-proton's signals. The values of "mean differential parameters" $\Delta\delta_i^{H,N}$ were calculated.

Keywords: NMR ^{1}H spectra, disubstituted para-alkylaromatic compounds , ortho- and meta-protons chemical shift, α-effect, β-effect, basic and differential spectral parameters, mean differential parameters.

# I. Introduction

It was shown that in NMR $^1$H spectra of monoalkylbenzenes [1] (including those containing functional groups in alkyl substituent [2]) and para-substituted alkylbenzenes [3], the basic spectral parameters $\delta^H_0$ – chemical shifts of nuclei of ortho-hydrogen atoms of phenyl ring (H-2 and H-6) – regularly depend upon the volume of space occupied by alkyl substituent in the definite place of alkyl chain. Thus, if the change of alkyl substituent volume occurring as a result of alkyl chain branching, takes place at $\alpha$-carbon atom, the change of $\delta^H_0$ value is called $\alpha$-effect; if the branching takes place at $\beta$-carbon atom, $\beta$-effect is observed. Sometimes in the name of $\alpha$- and $\beta$-effects the influenced atom is pointed, e.g. *ortho*-$\alpha$-effect or *meta*-$\beta$-effect. The positive value is attributed to *ortho*- $\alpha$-effect because $\delta^H_0$ value increases with the increase of amount of methyl groups introduced into $\alpha$-position. And on the contrary, the negative sign is attributed to *meta*-$\beta$-effect by the same reason.

It is of great interest to clear up whether the mentioned effects (*ortho*- and *meta*, $\alpha$- and $\beta$-) appear in NMR $^1$H spectra of disubstituted aromatic compounds, where alkyl group is one of the substituents. The subject of this report is the study of influence of position and number of branching at $\alpha$- and $\beta$-carbon atoms of alkyl substituent chain in **disubstituted para-alkylaromatic compounds** of the general formula **$p$-Y-C$_6$H$_4$-Alk** on the values of **basic ($\delta^H_o$, $\delta^H_m$)** and **differential ($\Delta\delta^H_o$, $\Delta\delta^H_m$) spectral parameters** of nuclei of ortho- (H-2 and H-6)[1] and meta-hydrogen (H-3 and H-5) atoms of phenyl ring.

Both atoms of Alk and Y substituents connected with phenylene fragment -C$_6$H$_4$- in *para*-Y-C$_6$H$_4$-Alk compounds are situated in the plain of phenyl ring on the same straight line crossing the molecule centre. Both substituents are maximally outlying one from another in the space, their direct steric interaction is minimized, therefore they may affect each other mainly via the transfer of electronic effects by means of phenyl ring.

The influence of both substituents on the hydrogen atoms in ortho- and meta-positions of phenyl ring may have both steric and electronic components. It is logically to assume that the main (and may be the single) contribution in the steric component of alkyl substituent (Alk) influence on ortho- (H-2 and H-6) and meta-hydrogen (H-3 and H-5) atoms will be done by its volume in the definite point of the space out of phenyl ring. At the same time we may assume that influence of the same substituent Y in the row containing this substituent (see below) on spectral parameters of nuclei of H-2 and H-6

atoms (possibly H-3 and H-5, too) will be constant. It means that in such a case the changes inside the row will take place only in the structure of alkyl substituent. Hence, we may suppose that the constant influence of Y substituent will not change the value of differential parameters $\Delta\delta^H_o$ and $\Delta\delta^H_m$ in such rows.

### I.1. Construction principles of comparable compounds rows (series).

To compare the spectral parameters of different compounds we use previously developed [1, 2] approach based on virtual division of investigated molecule into two fragments: "invariable" and "variable". We investigated the changes of differential spectral parameters taking place in that part of "invariable" fragment we are interested in under the influence of structural change of "variable" fragment. To our mind differential spectral parameters $\Delta\delta^H_o$ and $\Delta\delta^H_m$ are the best quantitative measures of α- and β-effects in NMR $^1$H spectra of alkylbenzenes.

By analogy with described earlier conception for monoalkylbenzene [1, 2] disubstituted compounds **p-Y-C$_6$H$_4$-Alk** are divided into two types depending upon the place of branching of alkyl chain in the substituent Alk: compounds of "A" type (branching occurs at α-carbon atom) and compound of "B" type (branching occurs at β-carbon atom). The same as previously [1-3] we chose substituents Alk containing maximally short alkyl chains: in the compounds of "A" type they contain 1 or 2 carbon atoms, in the compounds of "B" type – 2 or 3 carbon atoms.
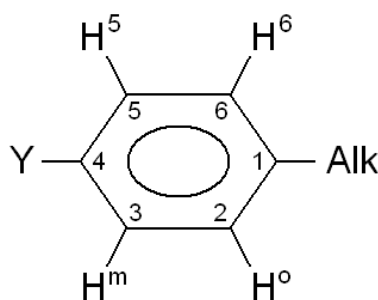
### I.1.1. Compounds of "A" type

Every row of the compounds of "A" type containing the same substituent Y is denoted by the general formula $\boldsymbol{p\text{-}Y\text{-}C_6H_4\text{-}C^{\alpha}R^1R^2R^3}$. The "invariable" fragment in the compounds of "A" type is $Y\text{-}C_6H_4\text{-}C^{\alpha}\equiv$. Three variable fragments $R^1$, $R^2$, $R^3$ are attached to it and denoted by italic. The **variable** fragments are **hydrogen atoms or methyl groups**. The amount of methyl groups among variable substituents we denote by "n" symbol; maximum value of $n_m$ is equal to three ($R^1=R^2=R^3$=Me; $n_m = 3$). The amount of terms (M) in complete [2] row is calculated by the formula: $M = n_m + 1 = 4$. The complete row of alkyl substituents of "A" type consists of 4 terms denoted by symbol "j": 1) Alk = Me, (n = 0, and $R^1 = R^2 = R^3$ = H, in formulae **1-21** j = a), 2) Alk = Et (n = 1, j = b), 3) Alk = Pr$^i$  (n = 2, j = c) and 4) Alk = Bu$^t$ (n = 3, j = d). Incomplete rows contain two or three terms; under necessity they may be transformed into "adjusted complete rows" by the procedure described in [2].

### I.1.2. Selection criteria for rows of $\boldsymbol{p\text{-}Y\text{-}C_6H_4\text{-}C^{\alpha}R^1R^2R^3}$ of "A" type

Among the variety of different functional groups which may be the substituents "Y" in disubstituted compounds **para-Y-C$_6$H$_4$-Alk** we examined first of all those 26

substituents which were studied earlier at the investigation of dependence of basic spectral parameters $\delta^H_i$ upon the substituent nature in monoalkylbenzenes [4, 5]. Hydrogen atom is included too, as "Y" substituent in para-position in monoalkylbenzenes. All ***para-Y-C₆H₄-Alk*** compounds involved we denote by symbol "**N**i" depending upon the substituent "Y" nature. Number **N** (**N** = 1–21) is given by bold and determines a row of compounds containing the same substituent "Y". As it was mentioned above letter "j" denotes the type of alkyl substituent Alk: j = a-d.



**1-21**

where Y = NMe₂ (**1**), NH₂ (**2**), OH (**3**), OMe (**4**), Me (**5**), Et (**6**), Pr$^i$ (**7**), Bu$^t$ (**8**), Ph (**9**), H (**10**), Br (**11**), COOH (**12**), COOMe (**13**), Ac (**14**), CH=O (**15**), NO₂ (**16**), OAc (**17**), CH₂Cl (**18**), CH₂Br (**19**), EtC=O (**20**), SO₂Cl (**21**).

Unfortunately, because of the insufficient amount of spectral data for the compounds of "A" type in [6] and [7] (see about them below) we were not able to make a complete four-termed rows for all supposed 26 rows. So we made 16 rows (complete or incomplete). Complete four-termed rows (**Na-Nd**) are given only for 7 above-mentioned substituents "Y" in the compounds **Y-C₆H₄-Alk**: NH₂ (compounds **2a-2d**), OH (**3**), Me (**5**), Ph (**9**), H (**10**), COOH (**15**), CH=O (**19**). For 9 of 17 remaining substituents "Y" which were discussed in [4, 5] we had to give incomplete rows in Table 1: NMe₂ (**1**), OMe (**4**), Et (**6**), Pr$^i$ (**7**), Bu$^t$ (**8**), Br (**13**), COOMe (**14**), Ac (**15**), NO₂ (**16**). We also could not make even most simple (two-term) incomplete rows for the compounds with 10 substituents "Y": OPh, SMe, SiMe₃, F, Cl, I, COOEt, CN, CF₃, SO₂Me.

But at the same time we found in [6, 7] spectral data for para-disubstituted benzenes with other five substituents "Y" which were not included to the mentioned 26 ones. The additional rows of compounds ***para-Y-C₆H₄-Alk,*** where Y=OAc (**17**, complete row), and incomplete rows, where "Y": CH₂Cl (**18**), CH₂Br (**19**), EtC=O (**20**) и SO₂Cl (**21**) are represented in Table 1 as well. For the systematization of data of NMR ^{1}H spectra we present here the complete rows of monoalkylbenzenes C₆H₅-Alk (**10**) which were analyzed earlier [1, 2]: compounds of "A" type (**10**a-d) and compounds of "B" type (**10**e-h,I).

The compounds of "B" type are discussed below.

## II. Experimental data

### II.1. Basic spectral parameters

### II.1.1. Introduced symbols and informational sources

Basic spectral parameters in NMR $^1$H spectra of para-disubstituted benzenes are denoted generally by symbols $\delta_i^{H,Nj}$. The superscript means: a) spectrum type ("H" – protonic); b) number of compound (**N**); c) type of alkyl substituent "j". In the subscript the symbol "i" denotes the position of hydrogen atom spectrum of which is studied in the phenyl ring (i=ortho or i=meta). In some cases the superscript contains number of literature source in square brackets and subscript contains the compound type: "$\alpha$" for the compounds of A type and "$\beta$" – for the compounds of "B" type, e.g. $\delta_{o,\alpha}^{H,3d[6]}$.

The selection of spectral data sources [1, 2] is based on the consideration of their availability and compatibility, criteria of which were examined earlier in [8]. We used $\delta_i^{H,Nj}$ values obtained in deuterochloroform as a solvent. They are given in references [6, 7]. Using only CDCl$_3$ as the solvent is conditioned by the possible dependence of $\delta^H$ values upon the solvent nature. Comparing the small changes in the values of basic spectral parameters $\delta^H$ as a result of supposed spatial interaction of molecule fragment, it is actually impossible to take into account greater changes which may be caused by different nature of the solvents. Therefore, in this paper we did not investigate spectra obtained in other solvents (for example, DMSO-d$_6$).

The peculiarities of basic spectral parameters used for the calculations of differential parameters in the compounds **1-21** are the same as those described for monoalkylbenzenes [1, 2].

### II.1.2. Signals attribution in NMR $^1$H spectra

In Ref. [6] in all cases there are author's attribution of doublet signals of NMR $^1$H spectrum to the corresponding values $\delta_i^{H,Nj}$ for two ortho- and two meta-protons. As far as in Ref. [7] the signals attribution is absent we fulfilled it by ourselves. Usually the values of $\delta_i^{H,Nj[6]}$ parameters given in [6] and $\delta_i^{H,Nj[7]}$ parameters given in [7] agree between each other. The difference between them rarely exceeds 0.020 ppm. The latter value is accepted as experimental mean error (accuracy of measurements), i.e. accuracy of $\delta_i^{H,Nj}$ parameters determination.

In some cases, due to the closeness of values $\delta_o^{H,Nj}$ and $\delta_m^{H,Nj}$ which differ between each other by size of order 0.010 ppm, the unambiguous attribution of mentioned signals is

difficult. The authors [6] of such signals attribution assume that they may be interchanged. In such a case we did not calculate differential parameters and put dash in the Table.

Basic spectral parameters $\delta_i^{H,Nj[6]}$ given in [6] were obtained using instruments with various frequency: at low-frequency instrument (90 MHz) and high-frequency instrument (400 MHz). In those cases when both values of $\delta_i^{H,Nj}$ are given in [6] and they are different, we used only value obtained by means of high-frequency instrument. "Low-frequency" parameter was used for the calculations of differential parameters only in the absence of "high-frequency" parameter.

Table 1 represents the basic spectral parameters $\delta_o^{H,Nj}$ and $\delta_m^{H,Nj}$ only for para-methylsubstituted benzenes $p$-**Y**-**C$_6$H$_4$**-**Me** (**1a-21a**). For other types of substituents (**1j-21j**, where: j = b,c,d) the differential parameters $\Delta\delta_o^{H,Nj}$ and $\Delta\delta_m^{H,Nj}$ are given in corresponding cells.

## II.2. Differential spectral parameters $\Delta\delta_i^{H,Nj}$

The differential spectral parameters $\Delta\delta_i^{H,Nj}$ were calculated using formula (1) from [2]:

$$\Delta\delta_i^{H,Nj} = \delta_i^{H,Nj} - \delta_i^{H,Na} \tag{1}$$

where $\delta_i^{H,Nj}$ is a basic spectral parameter in those para-disubstituted benzenes, in which substituent "Alk" is not a methyl group (Alk ≠ Me), i.e. $\delta_i^{H,Nj} \neq \delta_i^{H,Na}$

## II.2.1. Introduced symbols

The values of differential spectral parameters $\Delta\delta_i^{H,Nj}$ are represented in the Table. Every cell of the Table has two values of $\Delta\delta_i^{H,Nj}$ differential parameter given as a column: the upper value is calculated by formula (1) using basic parameters $\Delta\delta_i^{H,Nj[7]}$ and bottom value – using parameter $\Delta\delta_i^{H,Nj[6]}$. The upper digit is usual, the bottom one is bold; both digits are without brackets.

In those cases when the value of basic spectral parameter $\delta_i^{H,Nj}$ is absent in Refs. [6] or [7], it is impossible to calculate the value of corresponding differential parameter. To increase the statistic amount of data we calculated so called "crossed" differential parameter instead of mentioned one. The "crossed" parameter is calculated with simultaneous use of Refs. [6] and [7] data and placed in the cell instead of absent "uncrossed" value. "Crossed" differential parameters are denoted by bold in parentheses. For example, "crossed' parameter may be calculated by formula: $(\Delta\delta_o^{H,Nj})$ = $\delta_o^{H,Nj[7]} - \delta_o^{H,Na[6]}$, or on the contrary: $(\Delta\delta_o^{H,Nj}) = \delta_o^{H,Nj[6]} - \delta_o^{H,Na[7]}$.

Discussing the results we prefer parameters $\Delta\delta_i^{H,Nj[7]}$ compared with $\Delta\delta_i^{H,Nj[6]}$. The reason is that we have the possibility to control signals $\Delta\delta_i^{H,Nj[6]}$ attribution given by authors [6] and represented in [7] by means of scale enlarging of the spectrum part interesting for us. Thus we diminish the risk of errors which may be committed by authors [6].

As far as we assumed that reliability and accuracy of both "uncrossed" differential parameters $\Delta\delta_i^{H,Nj[7]}$ and $\Delta\delta_i^{H,Nj[6]}$ are considerably higher than accuracy of corresponding "crossed" parameters ($\mathbf{\Delta\delta_i^{H,Nj}}$), also taking into account that "crossed" parameters are represented in the Table only because of impossibility to calculate corresponding "uncrossed" differential parameters, their own valuables are low. If the value of "crossed" differential parameter does not practically differ from the value of the second parameter presented in the cell (i.e. $\Delta\delta_i^{H,Nj[7]}$ or $\Delta\delta_i^{H,Nj[6]}$), the "crossed" parameter serves only for confirmation: in other case the values of "crossed" differential parameters are not taken into account.

## II.3. Structure of Table 1

Spectral values for two ortho- and two meta-protons of phenyl ring of "A" type compound (**1-21**) by general formula $p\text{-}Y\text{-}C_6H_4\text{-}C^\alpha R^1 R^2 R^3$ are represented in Table 1. The structure of every cell is described above.

The first of four columns contains the values of basic spectral parameter ($\delta_o^{H,Na}$ or $\delta_m^{H,Na}$) and next three contain differential spectral parameters $\Delta\delta_i^{H,Nj}$ (where j = b,c,d) calculated by formula (1)**.** The values of basic spectral parameters $\delta_i^{H,Nj}$ (except $\delta_i^{H,Na}$ parameter) are minuends in formula (1) and are absent in Table 1. They may be calculated by adding of corresponding differential parameter with basic spectral parameter $\delta_i^{H,Na}$ which is subtrahend.

As it was mentioned above, the most reliable data are basic spectral parameters $\delta_i^{H,Nj[7]}$ obtained at "high-frequency" instrument of 300 MHz and parameters $\delta_i^{H,Nj[6]}$ obtained at the instrument with 400 MHz. The values of both types (experimental basic $\delta_i^{H,Na}$ and calculated differential $\Delta\delta_i^{H,Nj}$) are given with the accuracy of 0.001 ppm. The basic parameters $\delta_i^{H,Nj[6]}$ obtained at the instrument with 60 MHz which are given in square brackets are also involved. Their values are given in [6] with the accuracy of 0.01 ppm.

Table 1

Values of basic ($\delta_i^{H.Na}$) and differential ($\Delta\delta_i^{H.Nj}$) spectral parameters of compounds **1-21**

| Number of row | Substituent Y | Parameters of *ortho*-protons | | | | Parameters of *meta*-protons | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta_o^{H.Na}$ | $\Delta\delta_o^{H.Nb}$ | $\Delta\delta_o^{H.Nc}$ | $\Delta\delta_o^{H.Nd}$ | $\Delta_m^{H.Na}$ | $\Delta\delta_m^{H.Nb}$ | $\Delta\delta_m^{H.Nc}$ | $\Delta\delta_m^{H.Nd}$ |
| **1** | NMe$_2$ | 7.035; [**7.020**] | - | - | 0.230; **0.234** | 6.665; [**6.665**] | - | - | +0.040; **+0.038** |
| **2** | NH$_2$ | 6.940; **6.950** | 0.025; **0.010** | 0.065; **0.040** | 0.225; **0.214** | 6.565; **6.579** | +0.020; **0.000** | +0.040; **-0.011** | +0.040; **+0.019** |
| **3** | OH | -  7.**028** | (**0.007**); **0.036** | (**0.047**); **0.067** | (**0.217**) - | 6.731; [**6.721**] | (+**0.014**; +**0.027** | (+**0.029**; +**0.035** | (+**0.039**) - |
| **4** | OMe | 7.065; [**7.05**] | - | (**0.058**); **0.073** | (**0.225**); **0.240** | 6.785; [**6.780**] | - | (**0.035**); +**0.040** | (+**0.055**); +**0.060** |
| **5** | Me | 7.040; **7.046** | 0.035; (**0.029**) | 0.080; (**0.074**) | 0.235; (**0.214**) | 7.04; **7.046** | +0.035; +**0.034** | +0.060 - | +0.060; +**0.064** |
| **6** | Et | 7.075 - | 0.035; (**0.035**) | - | - | 7.075 - | +0.035; (+**0.035**) | - | - |
| **7** | Pr$^i$ | 7.090 - | - | 0.060; (**0.057**) | - | 7.12 - | - | +0.030; (+**0.027**) | - |
| **8** | Bu$^t$ | 7.100; [**7.110**] | - | - | 0.210; **0.210** | 7.275; (**7.260**) | - | - | +0.035; +**0.060** |
| **9** | Ph | 7.215; **7.249** | 0.030; **0.011** | 0.060; **0.011** | (**0.246**) 0.212 | 7.475; **7.493** | +0.020; +**0.015** | +0.030; +**0.005** | +0.057; (+**0.039**) |
| **10** | H | 7.145 - | 0.035 - | 0.070; (**0.086**) | 0.245 - | 7.23 - | +0.030 - | +0.040; (+**0.059**) | +0.060 - |
| **11** | Br | 7.020 - | 0.020; (**0.011**) | - | 0.215; (**0.214**) | 7.345 - | +0.025; (+**0.019**) | - | +0.050; (+**0.041**) |
| **12** | COOH | 7.265 - | -  (**0.025**) | 0.055; (**0.055**) | -  (**0.232**) | 8.01 - | -  (**0.028**) | +0.040; (+**0.040**) | -  (+**0.037**) |
| **13** | COOMe | 7.215; [**7.230**] | - | - | 0.230; **0.218** | 7.920; [**7.920**] | - | - | 0.045; **0.043** |
| **14** | Ac | 7.235; **7.228** | 0.030; **0.045** | - | - | 7.845; **7.838** | +0.030; +**0.033** | - | - |
| **15** | CH=O | 7.310; [**7.320**] | 0.035; **0.020** | 0.065; **0.060** | (**0.237**); **0.227** | 7.755; [**7.760**] | +0.040; +**0.020** | +0.050; +**0.040** | (+**0.061**); +**0.056** |
| **16** | NO$_2$ | 7.310; [**7.312**] | 0.025; (**0.023**) | 0.065; **0.067** | - | 8.095; [**8.098**] | +0.030; (+**0.027**) | +0.040; +**0.042** | - |
| **17** | OCOCH$_3$ | 7.145; [**7.140**] | (**0.019**); **0.024** | (**0.055**); **0.060** | (**0.225**); **0.230** | -  [**6.960**] | -  +**0.013** | -  +**0.025** | -  +**0.040** |
| **18** | CH$_2$Cl | 7.135 - | - | - | 0.240; (**0.215**) | 7.25 - | - | - | +0.055; (+**0.050**) |
| **19** | CH$_2$Br | 7.130; [**7.130**] | - | - | 0.225; (**0.225**) | 7.265; [**7.250**] | - | - | +0.045 - |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| **20** | EtCO | 7.235 <br> - | **-** <br> **(0.028)** | - | - <br> **(0.229)** | 7.855 <br> - | **-** <br> **(+0.030)** | - | **-** <br> **(+0.055)** |
| **21** | SO$_2$Cl | 7.410 <br> - | - | - | 0.225; <br> **(0.218)** | 7.915 <br> - | - | | +0.040; <br> **(+0.047)** |

## II.4. Compounds of "B" type

The compounds of "B" type are denoted by the general formula $Y\text{-}C_6H_4\text{-}C^{\alpha}Z^1Z^2\text{-}C^{\beta}R^1R^2R^3$, where symbol "Z" denotes hydrogen atom or methyl group[i]. The fragment $Y\text{-}C_6H_4\text{-}C(Z^1Z^2)\text{-}C^{\beta}\equiv$ is invariable and three variable fragments $R^1$, $R^2$, $R^3$ are attached to β-carbon atom.

The compounds of "B" type **1-21** have three variants of values $Z^1$ and $Z^2$: a) $Z^1 = Z^2 = H$; b) $Z^1 = H$, $Z^2 = Me$; c) $Z^1 = Z^2 = Me$. The complete row of four compounds may be developed for every of them (M=4).

In the first case (when $Z^1 = Z^2 = H$) the complete row includes following alkyl groups presented in Table 2: ethyl (Et, n=0, denoted by symbol "b" taken from Table 1); n-propyl (Pr, n=1, denoted by symbol "e", differential parameter is determined by the difference e-b); isobutyl (Bu$^i$, n=2, «f», «f-b»); neopentyl (Am$^{neo}$, n=3, «g», «g-b»).

In the second case, when $Z^1 = H$, $Z^2 = Me$, the following alkyl groups are examined in Table 2: isopropyl (Pr$^i$, n=0, «c») and secondary-butyl (Bu$^s$, n=1, «h», «h-c»). Spectral data for the other compounds of this row, i.e. compounds with alkyl substituents containing two ($R^1 = R^2 = CH_3$, $R^3 = H$, n=2) - the third term, or three methyl groups - the fourth term of complete row are absent in [6, 7].

The same situation takes place in the third case ($Z^1 = Z^2 = Me$), where only for tert-butyl (Bu$^t$, n=0, «d») and tert-amyl (Am$^t$, n=1, «k», «k-d») alkyl groups the spectral data are found. Therefore, in Table 2 we are forced to give incomplete rows in most of the cases. Moreover, often they consist of only two first terms of the row.

### II.4.1. Structure of Tables 2 and 3

Tables 2 and 3 represent values of basic ($\delta_i^{H,Nj}$) and calculated from them ($\Delta\delta_i^{H,Nj}$) spectral parameters for ortho- and meta-protons in 11 rows of the compounds of "B" type **2-17** with alkyl groups e,f,g,h and k. The symbols, cells structure and print type are the same as in Table 1.

Table 2

Values of basic ($\delta_o^{H,Nj}$) and differential ($\Delta\delta_o^{H,Nj}$) spectral parameters of ortho-protons in the compounds of "B" type **2-17** (Alk = $-C^\alpha Z^1 Z^2 - C^\beta R^1 R^2 R^3$)

| Number of row | Substituent Y | Basic spectral parameters of protons of the first term of the row | | | Differential spectral parameters of protons of the second-forth terms of the row | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta_o^{H,Nb}$ | $\delta_o^{H,Nc}$ | $\delta_o^{H,Nd}$ | $\Delta\delta_o^{H,Ne}$ (e-b) | $\Delta\delta_o^{H,Nf}$ (f-b) | $\Delta\delta_o^{H,Ng}$ (g-b) | $\Delta\delta_o^{H,Nh}$ (h-c) | $\Delta\delta_o^{H,Nk}$ (k-d) |
| 2 | NH$_2$ | 6.965; [6.960] | 7.005; 6.990 | - | -0.020; -0.024 | | - | -0.050; (-0.035) | - |
| 3 | OH | 7.035; 7.064 | 7.075; 7.095 | 7.245 - | -0.020; -0.030 | | - | (-0.049); -0.069 | -0.070; (-0.065) |
| 4 | OMe | - | - 7.123 | - | - | - | - | - -0.046 | - |
| 5 | Me | 7.075 - | - | - | - (-0.015) | - | - | - | - |
| 10 | H | 7.180 - | 7.210; 7.231 | 7.385 - | -0.020 - | - (-0.040) | -0.070 - | -0.040; (-0.061) | - (-0.075) |
| 11 | Br | 7.040; 7.031 | | - | -0.015; -0.019 | - | - | - | - |
| 12 | COOH | - 7.290 | | - | (-0.025); -0.019 | - | | - | - |
| 14 | Ac | 7.265; [7.273] | - | - | - | (-0.046); -0.054 | - | - | - |
| 15 | CH=O | 7.345; [7.340] | - | - | - | (-0.055); -0.050 | - | - | - |
| 16 | NO$_2$ | - | 7.375; 7.379 | - | - | - | - | (-0.046); -0.050 | - |
| 17 | OAc | - | - 7.200 | - | - | - | - | - -0.044 | - |

Table 3

Values of basic ($\delta_m^{H,Nj}$) and differential ($\Delta\delta_m^{H,Nj}$) spectral parameters of meta-protons in the compounds of "B" type **2-17** (Alk = $-C^\alpha Z^1 Z^2 - C^\beta R^1 R^2 R^3$)

| Number of row | Substituent Y | Basic spectral parameters of protons of the first term of the row | | | Differential spectral parameters of protons of the second-forth terms of the row | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | $\delta_m^{H,Nb}$ | $\delta_m^{H,Nc}$ | $\delta_m^{H,Nd}$ | $\Delta\delta_m^{H,Ne}$ (e-b) | $\Delta\delta_m^{H,Nf}$ (f-b) | $\Delta\delta_m^{H,Ng}$ (g-b) | $\Delta\delta_m^{H,Nh}$ (h-c) | $\Delta\delta_m^{H,Nk}$ (k-d) |
| 2 | NH$_2$ | 6.585; [6.579] | 6.605; 6.568 | - | 0.000; -0.016 | | - | 0.000; (+0.037) | - |
| 3 | OH | 6.745; 6.758 | 6.760; 6.766 | **6.770** - | 0.000; -0.009 | | - | (+0.003); -0.003 | 0.000 - |

| 4 | OMe | - | -<br>**6.820** | - | - | - | - | -<br>**+0.003** | - |
|---|---|---|---|---|---|---|---|---|---|
| 5 | Me | 7.075;<br>[7.080] | - | - | (-0.015);<br>-0.020 | - | - | - | - |
| 10 | H | 7.260<br>- | 7.270;<br>**7.289** | 7.290<br>- | -0.010<br>- | +0.006 - | -0.010<br>- | 0.000;<br>(-0.019) | 0.000<br>- |
| 11 | Br | 7.37;<br>**7.364** | - | - | 0.000;<br>**-0.004** | - | - | - | - |
| 12 | COOH | **-8.038** | - | - | (-0.003);<br>-0.003 | - | - | - | - |
| 14 | Ac | 7.265;<br>[7.273] | - | - | - | (-0.003);<br>**-0.003** | - | - | - |
| 15 | CH=O | 7.875;<br>[7.871] | - | - | - | (-0.003);<br>**+0.001** | - | - | - |
| 16 | NO$_2$ | - | 7.795;<br>[7.780] | - | - | - | - | (-0.006);<br>**+0.009** | - |
| 17 | OAc | - | **6.985** | - | - | - | - | **+0.004** | - |

# III. Results and Discussion

## III. 1. Averaged ("mean") values of differential parameters

For the analysis of dependence of differential parameters $\Delta\delta_{o,\alpha}^{H,Nj}$, $\Delta\delta_{o,\beta}^{H,Nj}$, $\Delta\delta_{m,\alpha}^{H,Nj}$ and $\Delta\delta_{m,\beta}^{H,Nj}$ upon the position and numbers of branching in alkyl substituent Alk (see Tables 1-3) it is advisable to use arithmetic mean value of every differential parameter. Such parameters we call "mean".

Symbols. Mean differential parameters in general we denote as "$\Delta\delta_i^j$". The superscript of mean parameters compared with individual parameters of particular compound ($\Delta\delta_i^{H,Nj}$) does not contain spectrum type (H) and number of compounds (**N**). After superscript letter "j" (see above) there may be a digit which designates value n – amount of methyl groups among substituents $R^1$, $R^2$, $R^3$. The subscript contain first letter - the symbol designating the position of hydrogen atoms in phenyl ring (ortho- or *meta*-). A type of compound also may be shown ("α" or "β"), e.g. $\Delta\delta_{o,\alpha}^{c(2)}$ and $\Delta\delta_{m,\beta}^{g(1)}$.

Mean differential parameters calculated for the compounds **1-21** of "A" type we denote as "α-type parameters" (i.e. $\Delta\delta_{i,\alpha}^j$); the parameters **2-17** of "B" type – "β-type parameter" ($\Delta\delta_{i,\beta}^j$). Moreover, all mean differential parameters may be divided into another two types depending upon the position of investigated proton in phenyl ring, and they may be united by general title "*ortho*-parameters" or "*meta*-parameters". Then, for example, above-mentioned parameter $\Delta\delta_{o,\alpha}^{c(2)}$ belongs to the "*ortho*-α-type" and parameter $\Delta\delta_{m,\beta}^{g(1)}$ – to the parameters of "*meta*-β-type".

The value of every mean parameter $\Delta\delta_i^j$ is statistic by definition. To calculate mean parameters from the data of Tables 1-3 we used unequal amount of initial differential parameters $\Delta\delta_i^{\mathbf{H,N(j)}}$, which are called as "number of examples". They and given in the last column of Tables 4 and 5 (see below) in parentheses after mean value of corresponding parameter.

Obviously, the higher examples amount is used for the calculations, the more reliable its "statistic validation". The greatest amount of spectral data $\Delta\delta_i^{N(j)}$ is for the compounds of "A" type, therefore we used the greatest number of examples (from 11 to 17) to calculate the mean parameters $\Delta\delta_{o,\alpha}^j$ and $\Delta\delta_{m,\alpha}^j$. To calculate the mean parameters $\Delta\delta_{o,\beta}^j$ the maximum amount of available examples are significantly less (6).

Arbitrarily we admitted so minimum number of examples (5) which allows to consider the calculation of mean parameter as "statistically valid". Based on this criterion we consider all 6 mean parameters $\Delta\delta_{o,\alpha}^j$ and $\Delta\delta_{m,\alpha}^j$ for the compounds of "A" type as "statistically valid". At the same time we found only two "statistically valid" parameters, $\Delta\delta_{i,\beta}^e$ and $\Delta\delta_{i,\beta}^h$ namely (by 6 examples for every) for the compounds of "B" type.

Parameters $\Delta\delta_{i,\beta}^f$ (3 examples) and $\Delta\delta_{i,\beta}^k$ (2 examples) are considered as "statistically insufficiently valid" by the above-mentioned definition. Anyway we consider them as well, taking into account this drawback. In accordance with the same definition, parameter $\Delta\delta_{i,\beta}^g$ cannot be considered as "mean" because for its calculation it was possible to use spectral data of only one compound – 10g. However, for the sake of uniformity we'll examine this parameter as "mean" one and consider it as "statistically insufficiently valid".

Let us divide mean parameters into two groups by their absolute values. The first group contains parameters with "insignificant" absolute value and the second one – with "considerable" absolute value. The conditional boundary between them is determined by absolute values of mean parameters given in Tables 4 and 5. It is equal to threefold accuracy (error of measurements), i.e. 0.060 ppm.

## III.2. Structure of Tables 4 and 5

The results of calculations of mean differential parameters ($\Delta\delta_{i,}^j$) are given in the last column of Tables 4 and 5 by bold and larger type with the accuracy of 0.001 ppm. The sign is obligatory ("+" or "-"). After the digit there is a number of examples used for the calculation of mean value in parentheses.

In the forth (from the end) column there are intervals of values corresponding to the individual differential parameters $\Delta\delta_i^{N(j)}$ taken from Tables 1 and 2 and used for the

calculation of mean parameter $\Delta\delta_i^j$. Minimum and maximum values of $\Delta\delta_j^{N(i)}$ are called "boundary parameters" because they designate (bound) the interval. These digits are of regular font regardless of font type in Tables 1 or 2. After them the digit of compounds which determine the "boundary parameter" is given in parentheses by bold. "Crossed" values of "boundary parameters" are given in parentheses, the same as in Tables 1 and 2.

Then, the following two columns contain data concerning the interval width denoted by the symbol "$\Delta\Delta\delta_i^j$". The first column contains absolute value of interval width in ppm and denoted as $\Delta\Delta\delta_{i,abs.}^j$. The second column has relative values of interval width in percents and denoted as $\Delta\Delta\delta_{i,rel.}^j$. They are given only for "considerable" by absolute value mean parameters. Parameter $\Delta\Delta\delta_{i,rel.}^j$ is cal- culated as quotient of absolute interval width division by absolute value of "considerable" mean parameter, i.e. $\Delta\Delta\delta_{i,rel.}^j = \Delta\Delta\delta_{i,abs.}^j / \left| \Delta\delta_{i,}^j \right|$.

We symbolically divide the relative width of intervals by three types. The width of "narrow" interval does not exceed arbitrarily selected value of 20%. The "middle" interval has ratio: $20\% < \Delta\Delta\delta_{i,rel.}^j < 100\%$. The width of "wide" intervals is more than 100%. Apparently if we do not introduce limitations by value of mean parameter, the majority of intervals of "insignificant" mean parameters would be "wide" because of the small value of divisor comparable with dividend value. For "insignificant" parameters the column "Relative width of interval" has dash in Tables 4 and 5.

Table 4

Mean values of calculated differential parameters $\Delta\delta_o^j$ for *ortho*-protons in compounds **1-21**

| Compound type (number of Table) | Alkyl group (its lettering in Tables 1, 2, 3 | Value of "n" parameter | Minuend and subtrahend in formula: $\Delta\delta_o^j = \delta_o^j - \delta_o^{(0)}$ | Mean parameter $\Delta\delta_o^j$, ppm | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Symbol of mean parameter | Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**) | Absolute width of interval $(\Delta\Delta\delta_{o,abs.}^j)$, ppm | Relative width of interval $(\Delta\Delta\delta_{o,rel.}^j)$, % | Average value (number of examples in Tables 1 or 2,3 for calculations) |
| A (1) | Et (b) | 1 | b-a | $\Delta\delta_{o,\alpha}^b$ | from (0.007) (**3**) to 0.045 (**18**) | 0.038 | - | **+0.026** (13) |
| A (1) | Pr$^i$ (c) | 2 | c-a | $\Delta\delta_{o,\alpha}^c$ | from 0.040 (**2**) to | 0.046 | 73 (mid.) | **+0.063** (11) |

| | | | | | (0.086) (**10**) | | | |
|---|---|---|---|---|---|---|---|---|
| A (1) | Bu$^t$ (d) | 3 | d-a | $\Delta\delta_{o,\alpha}{}^d$ | from 0.210 (**8**) to (0.246) (**9**) | 0.036 | 16 (nar.) | **+0.225** (17) |
| B (2) | Pr (e) | 1 | e-b | $\Delta\delta_{o,\beta}{}^e$ | from -0.030 (**3**) to -0.015(**5,13**) | 0.015 | - | **-0.021** (6) |
| B (2) | Bu$^i$ (f) | 2 | f-b | $\Delta\delta_{o,\beta}{}^f$ | From (-0.055) (**18**) to -0.040 (**10**) | 0.015 | - | **-0.049** (3) |
| B (2) | Am$^{neo}$ (g) | 3 | g-b | $\Delta\delta_{o,\beta}{}^g$ | -0.070 (**10**) | - | - | **-0.070** (1) |
| B (2) | Bu$^s$ (h) | 1 | h-c | $\Delta\delta_{o,\beta}{}^h$ | from -0.069 (**3**) to (-0.035) (**2**) | 0.034 | - | **-0.049** (6) |
| B (2) | Am$^t$ (k) | 3 | k-d | $\Delta\delta_{o,\beta}{}^k$ | from (-0.075) (**10**) to (-0.065) (**3**) | 0.010 | 14 (nar.) | **-0.070** (2) |

Table 5

Mean values of calculated differential parameters $\Delta\delta_m{}^j$ for *meta*-protons
in compounds **2-17**

| Compound type (number of Table) | Alkyl group (its lettering in Tables 1, 2, 3) | Value of "n" parameter | Minuend and subtrahend in formula: $\Delta\delta_m{}^j = \delta_m{}^j - \delta_m{}^{(0)}$ | Mean parameter $\Delta\delta_m{}^j$, ppm | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | Symbol of mean parameter | Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**) | Absolute width of interval ($\Delta\Delta\delta_{m,abs.}{}^j$), ppm | Relative width of interval ($\Delta\Delta\delta_{m,rel.}{}^j$), % | Average value (number of examples in Tables 1 or 2,3 for calculations) |
| A (1) | Et (b) | 1 | b-a | $\Delta\delta_{m,\alpha}{}^b$ | from (0.000) (**3**) to 0.040 (**19**) | 0.040 | - | **+0.025** (13) |
| A (1) | Pr$^i$ (c) | 2 | c-a | $\Delta\delta_{m,\alpha}{}^c$ | from -0.011 (**2**) to 0.060 (**5**) | 0.071 | - | **+0.035** (11) |
| A (1) | Bu$^t$ (d) | 3 | d-a | $\Delta\delta_{m,\alpha}{}^d$ | from 0.019 (**2**) to 0.064 (**5**) | 0.045 | - | **+0.050** (17) |
| B (2) | Pr (e) | 1 | e-b | $\Delta\delta_{m,\beta}{}^e$ | from -0.020 (**5**) to 0.000 (**2,3,13**) | 0.020 | - | **-0.007** (6) |
| B (2) | Bu$^i$ (f) | 2 | f-b | $\Delta\delta_{m,\beta}{}^f$ | from -0.006 | 0.015 | - | **+0.001** |

| | | | | | (19) to +0.009 (**19**) | | | (3) |
|---|---|---|---|---|---|---|---|---|
| B (2) | $Am^{neo}$ (g) | 3 | g-b | $\Delta\delta_{m,\beta}^{g}$ | -0.010 (**10**) | - | - | **-0.010** (1) |
| B (2) | $Bu^{s}$ (h) | 1 | h-c | $\Delta\delta_{m,\beta}^{h}$ | from -0.019 (**10**) to 0.037 (**2**) | 0.056 | - | **+0.005** (6) |
| B (2) | $Am^{t}$ (k) | 1 | k-d | $\Delta\delta_{m,\beta}^{k}$ | from 0.000 (**3**) to 0.000 (**10**) | 0.000 | - | **0.000** (2) |

### III.3. Ratio between mean parameters by value and sign

All given in Tables 4 and 5 mean differential parameters $\Delta\delta_{i}^{j}$ we rounded to the values divisible by 0.005 ppm and represented as diagrams in Fig. 1 and 2.

Fig. 1.
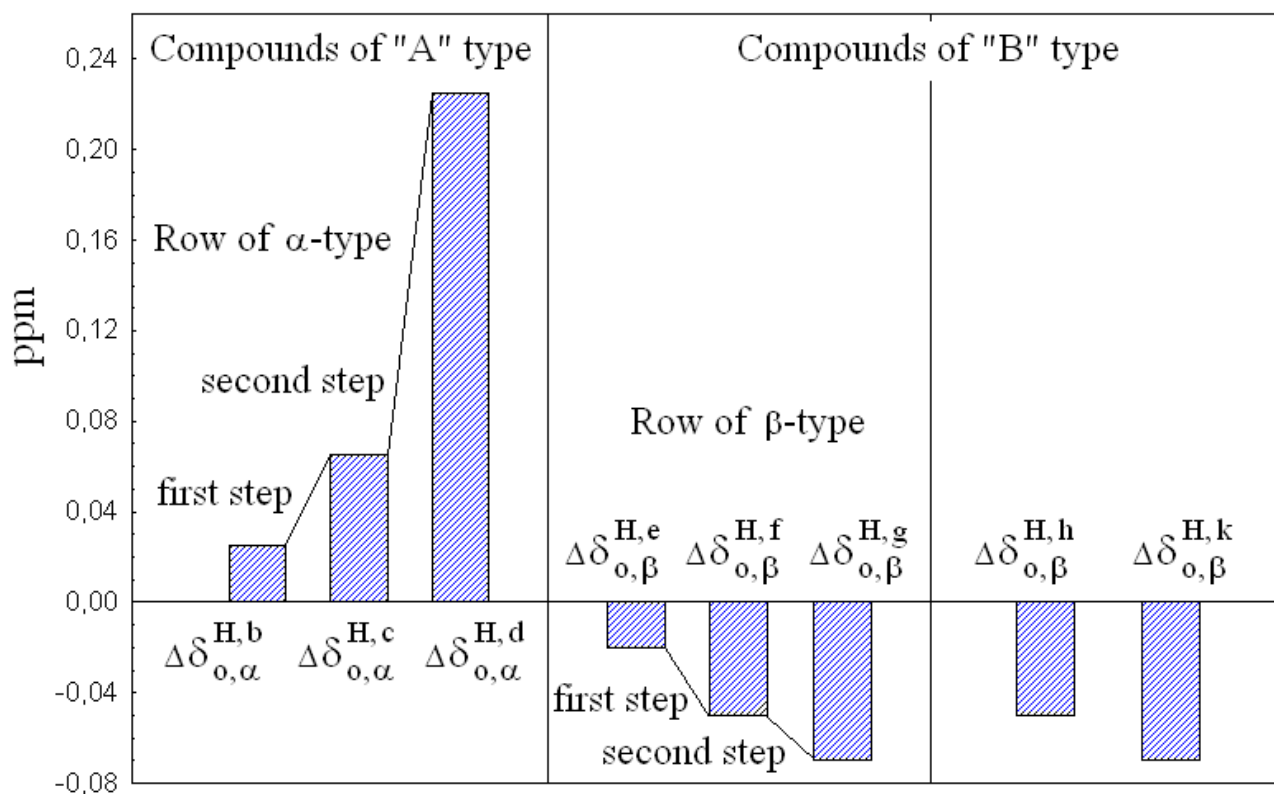


The values of mean differential parameters $\Delta\delta_{0}^{H,j}$

Fig. 2.
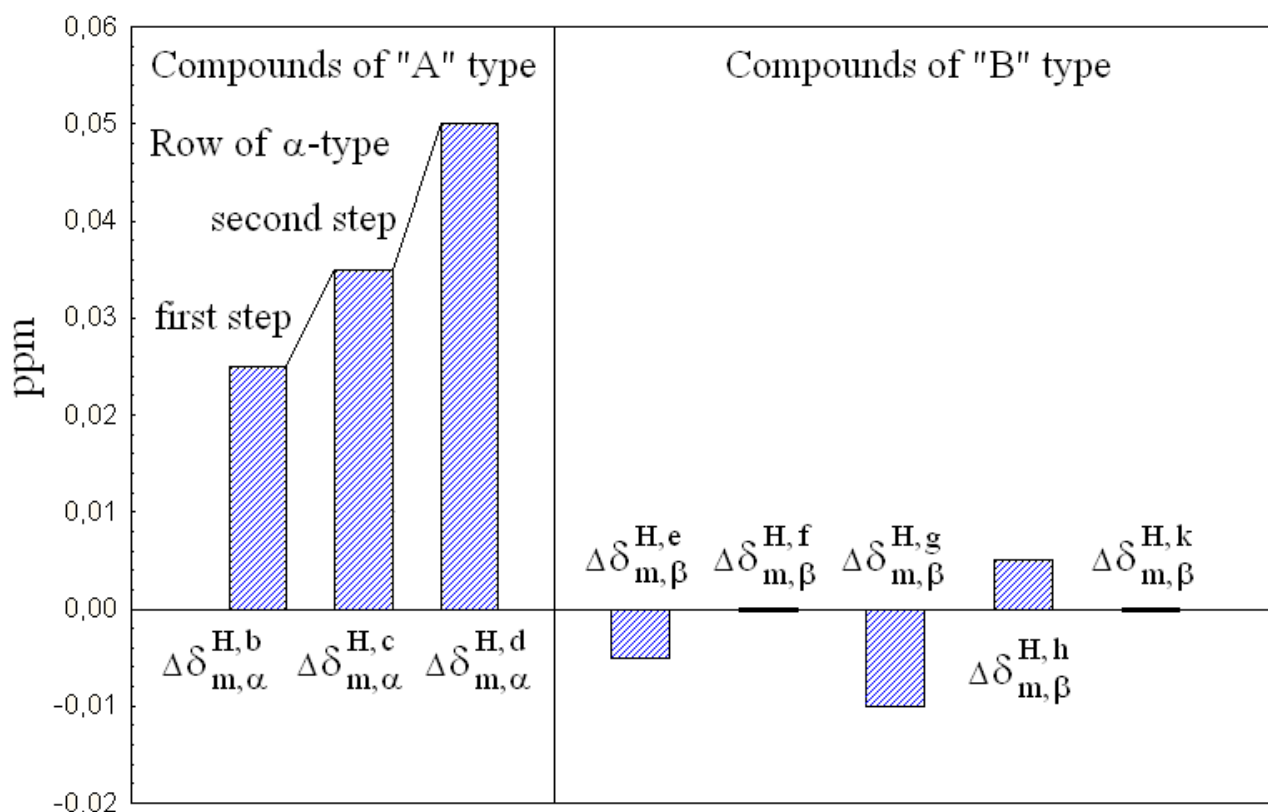


The values of mean differential parameters $\Delta\delta_m^{H,j}$

As we can see in table 5, absolute values of all 5 mean parameters of "*meta*-β-type" $\Delta\delta_{i,\beta}^{j}$ do not exceed 0.010 ppm, which is twice less than an experimental error and in 6 time less than the value of conditional boundary between "insignificant" and "considerable" parameters. Therefore the further examination of such mean parameters is to no purpose because of their small absolute value.

Having enough experimental data we would be able to construct all 8 possible three-termed rows of mean parameters: by four for *ortho*- and *meta*-protons. But now we can construct and discuss only 3 (of 8 possible) three-termed rows of mean parameters.

Two of this 3 rows represent α-type, i.e. $\Delta\delta_{i,\alpha}^{j}$: one for *ortho*-protons ($\Delta\delta_{o,\alpha}^{b(1)} \rightarrow \Delta\delta_{o,\alpha}^{c(2)} \rightarrow \Delta\delta_{o,\alpha}^{d(3)}$) and second for *meta*-protons ($\Delta\delta_{m,\alpha}^{b(1)} \rightarrow \Delta\delta_{m,\alpha}^{c(2)} \rightarrow \Delta\delta_{m,\alpha}^{d(3)}$). The third row represent parameters of β-type $\Delta\delta_{i,\beta}^{j}$. As it was mentioned above, we were able to construct 2 complete rows of parameters of β-type $\Delta\delta_{i,\beta}^{j}$: for ortho-protons ($\Delta\delta_{o,\beta}^{e(1)} \rightarrow \Delta\delta_{o,\beta}^{f(2)} \rightarrow \Delta\delta_{o,\beta}^{g(3)}$) and for *meta*-protons ($\Delta\delta_{m,\beta}^{e(1)} \rightarrow \Delta\delta_{m,\beta}^{f(2)} \rightarrow \Delta\delta_{m,\beta}^{g(3)}$). But the consideration of latter row is pointless because of small absolute values of its mean parameters (≤0.010 ppm).

Four other possible three-termed rows of β-type $\Delta\delta_{i.,\beta}{}^{j}$ parameters are limited only by first terms ($\Delta\delta_{o,\beta}{}^{h(1)}$, $\Delta\delta_{o,\beta}{}^{k(1)}$, $\Delta\delta_{m,\beta}{}^{h(1)}$ and $\Delta\delta_{m,\beta}{}^{k1)}$) because of the lack of experimental data and therefore cannot be considered as rows by definition.

Both rows of α-type parameters are "statistically valid" because every parameter in them is calculated from great (no less than 11) numbers of examples. Unfortunately the single discussed three-termed row of *ortho*-β-type parameters can not be considered as "statistically valid". The mean parameter $\Delta\delta_{o,\beta}{}^{f}$ in it is calculated from 3 examples (instead of 5 required) and the last parameter $\Delta\delta_{o,\beta}{}^{H,g}$ is accepted using data of only one compound – **10g**. The insufficient "statistic validation" makes the discussion results less valuable. Thus we compare only three of eight three-termed rows. Two of them are "statistically valid" and the third one – insufficiently "statistically valid". Moreover, we'll discuss mean parameters of first terms ($\Delta\delta_{o,\alpha}{}^{h(1)}$, $\Delta\delta_{o,\alpha}{}^{k(1)}$, $\Delta\delta_{m,\beta}{}^{h(1)}$ and $\Delta\delta_{m,\beta}{}^{k(1)}$) of four possible, but non-existent three-termed rows. The following summarizing may be done.

### III.3.1. Rows of α-type

### III.3.1.1. Row of mean parameters of *ortho*-α-type:
### $\Delta\delta_{o,\alpha}{}^{b(1)} = 0.025$ ppm $\rightarrow \Delta\delta_{o,\alpha}{}^{c(2)} = 0.065$ ppm $\rightarrow \Delta\delta_{o,\alpha}{}^{d(3)} = 0.225$ ppm

1.      All three parameters of the row have positive value (sign "+") and their absolute value increases in the row. Moreover, if the first parameter ($\Delta\delta_{o,\alpha}{}^{b(1)}$) is "insignificant", the last two terms are "considerable" ones. Let us note that the first transfer ($\Delta\delta_{o,\alpha}{}^{b(1)} \rightarrow \Delta\delta_{o,\alpha}{}^{c(2)}$) is sufficiently smooth because its value of 0.040 ppm is comparable with the values of mean parameters participating in the transfer (step). During the second (and the last) step (i.e. while transfer $\Delta\delta_{o,\alpha}{}^{c(2)} \rightarrow \Delta\delta_{o,\alpha}{}^{d(3)}$) there is a sharp jump of chemical shift value (0.160 ppm) which is almost three-times higher than one of the parameters ($\Delta\delta_{o,\alpha}{}^{c(2)}$).

2.      Absolute width of intervals of all three parameters is relatively constant and equal to 0.040 ppm. This value is relatively low compared with accepted value of accuracy (0.020 ppm). However the relative width of two "considerable " intervals given in Table 4 decreases from "middle" to "narrow". This phenomenon takes place due to the increase of divisor at constant dividend in the above-mentioned equation. The low value of relative width (14%) of the last mean parameter $\Delta\delta_{o,\alpha}{}^{d(3)}$ is of special interest. The narrowness of this interval allows to suppose that the effect of "Y" substituent nature in the compounds **1-21** is not a determining factor for the formation of chemical shift of *ortho*-protons (parameter $\delta_{o,\alpha}{}^{d(3)}$). The same assumption is logical with respect to other two parameters of the row: $\Delta\delta_{o,\alpha}{}^{b(1)}$ and $\Delta\delta_{o,\alpha}{}^{c(2)}$. Obviously, the main factor for the formation of basic spectral parameter $\delta_{o}{}^{j}$ – chemical shift of *ortho*-protons in *para*-

alkylsubstituted derivatives of benzene – is not nature of "Y" substituent but degree of alkyl chain branching at $\alpha$-carbon atom. Earlier [1] we suggested the reasons of such influence in the monoalkylbenzenes row.

### III.3.1.2. Row of mean parameters of *meta*-$\alpha$-type:
$$\underline{\Delta\delta_{m,\alpha}{}^{b(1)} = 0.025 \text{ ppm} \rightarrow \Delta\delta_{m,\alpha}{}^{c(2)} = 0.035 \text{ ppm} \rightarrow \Delta\delta_{m,\alpha}{}^{d(3)} = 0.050 \text{ ppm}}$$

1.      All three parameters of the row, the same as of the row of *ortho*-$\alpha$-parameter, have positive values (sign "+") and their absolute value also increases. However, the absolute values of all three parameters are "insignificant" because even the greatest of them ($\underline{\Delta\delta_{M,\alpha}{}^{d(3)}}$) is less than "boundary" value (0.060 ppm). In both steps of the row the increase is smooth (even more smooth than for the first step in the row of *ortho*-$\alpha$-parameter). The sharp jump observed at the second step for *ortho*-$\alpha$-parameters is absent here. The general "two-step" increase of chemical shift is 0.025 ppm, whereas the value of first ("little") step in the row of *ortho*-$\alpha$-parameters is almost twice higher.

2.      Absolute width of two of three intervals in the investigated row ($\Delta\Delta\delta_{m,abs.}{}^{b}$ и $\Delta\Delta\delta_{m,abs.}{}^{d}$) is equal to 0.040 ppm , the same as for the row of *ortho*-$\alpha$-parameters. Only interval $\Delta\Delta\delta_{m,abs.}{}^{c}$ is something wider (0.070 ppm). To our mind, the "widening" of this interval is caused by "erroneous" value of parameter $\Delta\delta_{m,\alpha}{}^{H,2c[6]}$ (-0.011 ppm) determined the high field boundary of this interval. Actually the width of $\Delta\Delta\delta_{m,abs.}{}^{c}$ interval should be comparable with above-mentioned value of 0.040 ppm typical for other five intervals of both rows[ii]. The relative width of intervals was not calculated because of the insufficient absolute value of mean parameters.

We may suppose that the main factor affecting the value of chemical shift of *meta*-protons is branching of alkyl chain at $\alpha$-carbon atom, the same as in a case of *ortho*-protons. However due to the greater moving off the branching point this effect is less.

### III.3.2. Rows of $\beta$-type

### III.3.2.1. Row of mean parameters of *ortho*-$\beta$-type:
$$\underline{\Delta\delta_{o,\beta}{}^{e(1)} = -0.020 \text{ ppm} \rightarrow \Delta\delta_{o\beta}{}^{f(2)} = -0.050 \text{ ppm} \rightarrow \Delta\delta_{o,\beta}{}^{g(3)} = -0.070 \text{ ppm}}$$

1.      All three parameters of the row, in contrast to the both above-mentioned rows of $\alpha$-parameters have negative value (sign "-"). But the absolute value increases, the same as in two previous rows. The first two terms in the row are "insignificant", the third one may be considered as "considerable" one. The general "two-step" increase of absolute value of chemical shift is 0.050 ppm, what is twice greater than that in the row of *meta*-$\alpha$-parameters. The increase is smooth, in contrast to the spasmodic increase in the row of *ortho*-$\alpha$-parameters. The absolute value of the last parameter $\Delta\delta_{o,\beta}{}^{g(3)}$ (as it was

mentioned higher, value of which is not statistic) is some higher than absolute value of the last term $\Delta\delta_{m,\alpha}^{d(3)}$ in *meta*-α-row, though these values are comparable between each other (0.070 and 0.050 ppm). It should be noted that the value of first ("little") step in the row of *ortho*-β-parameters is in 1.5 times greater than that of the second step (it is the same, as in the row of *meta*-α-parameters, but differ from *ortho*-α-parameters). Excluding the negative sign for the row of **ortho-β-parameters**, **similarity** with the row of **meta-α-parameters**, and essential distinction from the row of *ortho*-α-parameters are observed. The **explanation** is the **comparable distance** of investigated **proton in phenyl ring from the branching point in the chain** of alkyl substituent. In contrast to two "outlying" interactions (*meta*-α-row and *ortho*-β-row) the distance between *ortho*-proton and branching point in *ortho*-α-row is shorter by one C-C bond.

2.     It is advisable to consider the absolute width of intervals only on the case of the first parameter ($\Delta\Delta\delta_{o,abs.}^{e}$), because this parameter is "statistically valid". Its absolute width is three times less than that of above-mentioned values for *ortho*- and *meta*-α-rows (0.015 against 0.040 ppm) and even less than accuracy of measurements (0.020 ppm).

Because of the insufficient values of all three parameters of the row the relative width of their intervals is not given in Table 5. However due to the small absolute width of the first two intervals ($\Delta\Delta\delta_{o,abs.}^{e} = \Delta\Delta\delta_{o,abs.}^{f} = 0.015$ ppm), and in spite of "insignificant" values of parameters $\Delta\delta_{o,\beta}^{e(1)}$ and $\Delta\delta_{o,\beta}^{f}$, the relative width of these intervals are "middle" ($\Delta\Delta\delta_{o,rel.}^{e} = 71\%$ and $\Delta\Delta\delta_{o,rel.}^{f} = 31\%$).

### III.3.3. Mean parameters of the first terms of four possible, but non-formed rows: $\Delta\delta_{o,\beta}^{h(1)}$, $\Delta\delta_{o,\beta}^{k(1)}$, $\Delta\delta_{m,\beta}^{h(1)}$ and $\Delta\delta_{m,\beta}^{k1}$

As it was mentioned above, absolute values of *meta*-β-parameters are close to zero (Table 5), therefore *meta*-parameters $\Delta\delta_{m,\beta}^{h(1)}$ and $\Delta\delta_{m,\beta}^{k1}$ are not discussed here.

**Ortho-*parameters* $\Delta\delta_{o,\beta}^{h(1)}$ and $\Delta\delta_{o,\beta}^{k1}$**, represented in Table 4, as well as parameters of *ortho*-β-row discussed in this Subsection III.3.3. **have negative value** (sign "-"). Their rounded absolute values (0.050 and 0.070 ppm, relatively) are practically equal to the accepted boundary between "insignificant" and "considerable" parameters (0.060 ppm).

As far as these parameters would be the first terms of two non-formed rows (because of the lack of spectral data), it would be desirable to compare their values with the value of first term of *ortho*-β-parameters row (see Subsection III.3.2.) – parameter $\Delta\delta_{o,\beta}^{e} = -0.020$ ppm. The row of "first" parameters depends upon the degree of branching at α-carbon

atom ($\Delta\delta_{o,\beta}{}^{e(1)}$ = **-0.020 ppm** → $\Delta\delta_{o\beta}{}^{h(1)}$ = **-0.050 ppm** → $\Delta\delta_{o,\beta}{}^{k(1)}$ = **-0.070 ppm**). The increase of absolute value of corresponding parameter is observed in the row. The values of $\Delta\delta_{o,\beta}{}^{j(1)}$ parameters in this row (Ne→Nh→Nk) coincide with the values of corresponding parameters in *ortho*-β-row ($\Delta\delta_{o,\beta}{}^{j}$) of the compounds (Ne→Nf→Ng), where the branching occurs at β-carbon atom of alkyl chain. Hence we may suppose that the **branching of alkyl chain** (independent on its position in it: α- or β-) **increases the absolute value of mean parameter** (in our case with negative sign). However, this conclusion needs statistic examination.


## IV. Conclusions

1. Considering the great amount of rows of disubstituted para-alkylaromatic compounds of the general formula ***p*-Y-C$_6$H$_4$-Alk** we **confirmed and "statistically validate" the conclusions made in [1]** during investigations of alkylbenzenes C$_6$H$_5$-Alk. The **chain branching at α-carbon** atom leads to the **positive *ortho*-α-effect**; the **branching at β-carbon** atom – to the **negative *ortho*-β-effect**.

2. The **"statistically valid" conclusion** was done that chain **branching at α-carbon** atom leads to the **positive *meta*-α-effect**. Such conclusion was not done earlier in [1] because only one example of alkylbenzenes was insufficient.

3. We supposed that **quantitative effect of the branching at α-carbon** atom on the **chemical shift of *meta*-protons (*meta*-α-effect) is equal** by value and opposite by sign to the similar **influence of the branching at β-carbon atom (*ortho*-β-effect) on *ortho*-protons**. It means that **quantitative characteristics** of these effects are **determined by the number of carbon-carbonic bonds** between the **investigated proton and branching point** of alkyl chain. *Ortho*-α-effect (i.e. quantitative effect on *ortho*-protons at the branching at α-carbon atom) is considerably greater than two above-mentioned ones, because a number of C-C bonds in it is less by one.

4. *Meta*-β-effect was found to be negligible by value (or it is absent at all) because investigated *meta*-proton is too far from the branching point at β-carbon atom by one more C-C bond compared with insignificant by value *ortho*-β-effect.

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[i] The other values of "Z" symbol is possible (Z = -C$^{\beta}$R$^1$R$^2$R$^3$). These cases will be considered in the accompanied communication concerning NMR $^{13}$C spectra of para-alkylsubstituted benzenes, i.e. compounds of "B" type.

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