The effect of branching in alkyl substituents on the value of chemical shifts of nuclei of C-1 – C-4 atoms of phenyl ring in NMR ^{13}C spectra of monosubstituted para-alkylbenzenes.

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Abstract. The analysis of aromatic carbon nuclei chemical shifts in ^{13}C NMR spectra of 26 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 increase the number of methyl groups at α-carbon atom (α-effect) leads to a downfield shift absorption of ipso-carbon (positive ipso-α-effect), and upfield shift absorption of ortho-carbon (negative ortho-α-effect). When the introduction of methyl groups takes place to the β-carbon atom there is observed ipso- and meta-negative β-effects and positive ortho- β-effect. The values of “mean differential parameters” $\Delta\delta_i^{H,N}$ were calculated.

Keywords: NMR ^{13}C spectra, disubstituted para-alkylaromatic compounds ,ipso-, ortho-, meta- and para-carbon atoms, carbon chemical shift, α-effect, β-effect, basic and differential spectral parameters, mean differential parameters.

I. Introduction

In the previous work [1] we studied the effect of branching in alkyl substituents in *para*-alkylbenzenes of the general formula ***p*-Y-C_6H_4-Alk** on the value of chemical shifts of nuclei of H-2 and H-3 atoms of phenyl ring in NMR ^{1}H spectra. We showed that chain branching at α-carbon atom leads to the positive *ortho*-α-effect and *meta*-α-effect (shift of *ortho*- and *meta*-protons signals to the low field, relatively). The branching of chain at β-carbon atoms leads to the negative *ortho*-β-effect. At the same time *meta*-β-effect was too small by value (or it was absent at all) due to the outlying position of investigated *meta*-proton from the branching point of chain at β-carbon atom.

It is of great interest to examine whether mentioned α- and β-effects will appear in NMR ^{13}C spectra of the same compounds ***p*-Y-C_6H_4-Alk.** The subject of this report is the study of influence of position and number of branching at α- and β-carbon atoms of alkyl substituent on the values of **basic (δ_i^C)** and **differential** (**$\Delta\delta_i^C$**) **spectral parameters** of nuclei of *ipso*- (C-1), *ortho*- (C-2 and C-6), *meta*- (C-3 and C-5) and *para*- (C-4) carbon atoms of phenyl ring. Some previous results of the investigations have been published earlier [2].

Both Alk and Y substituents in 4-Y-C_6H_4-Alk compounds are situated on the same straight line which passes through the molecule centre at the maximum distance one from another. Therefore we may suppose that the influence of one substituent on the investigated carbon atom of phenyl ring would be independent from the influence of another; their summary effect would be additive. It means that at the constant structure of the second substituent Y in the specially selected series (rows) of compounds (see below) the observed changes in spectrum are caused by alkyl substituent only, i.e. the substituent Y (which is constant) will not affect the value of differential parameters $\Delta\delta_i^C$ inside the rows.

Let us divide the influence of both substituents on the carbon atoms of phenyl ring into steric and electronic components. It is logically to assume that the main (and may be the single) contribution to the **steric component of alkyl substituent (Alk)** influence on the spectral parameters of carbon atoms will be done by **its volume in the definite point of the space out of phenyl ring** [3-5]. The electronic component of the mentioned influence may be accepted as constant value because both constants of Hammet and Braun are slightly differed for alkyl substituents of different structure.

I.1. Construction principles of comparable compounds rows

To compare the spectral parameters of different compounds we use previously developed [1-4] approach based on virtual division of investigated molecule into two fragments: “invariable” and “variable” ones. 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 $\Delta\delta_i^C$ are the best quantitative measures of α- and β-effects in NMR ^{13}C spectra of alkylbenzenes.

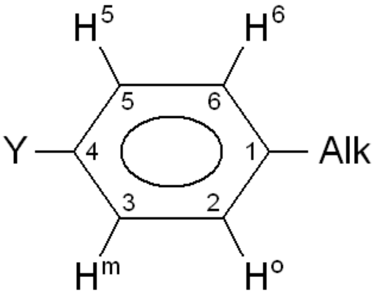
By analogy with described earlier conception for monoalkylbenzene [3,4] disubstituted compounds **4-Y-C_6H_4-Alk** are divided into two types depending upon the place of branching of alkyl chain in the substituent Alk: compounds of **“A” type (branching occurs at α-carbon atom)** and compound of **“B” type (branching occurs at β-carbon atom).** The substituents Alk contain 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.2. Compounds of “A” type

Every row of the compounds of “A” type containing the same substituent Y is denoted by the general formula ***p*-Y-C_6H_4-$C^{\alpha}R^1R^2R^3$.** The “invariable” fragment in the compounds of “A” type is 4-Y-C_6H_4-$C^{\alpha}\equiv$. 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 number 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 number of terms M in complete [3,4] 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, j = a in formulae **1-26**), 2) Alk = Et (n = 1, j = b), 3) Alk = Pr^i (n = 2, j = c) and 4) Alk = Bu^t (n = 3, j = d). The series containing **two or three terms** we call as **incomplete rows.**

I.1.2. Selection criteria for rows of 4-Y-C_6H_4-$C^{\alpha}R^1R^2R^3$ compound of “A” type

Among the variety of different functional groups which may be the substituents “Y” in ***para*-*Y*-C_6H_4-Alk** compounds we selected 26 substituents (including hydrogen atom) on account of reasons described in [1]. These substituents involve all range of electronic properties: from the most electron-donor substituents (of NR_2 and OR types) to the most electron-acceptor (NO_2 and SO_2Cl) ones. All **4-*Y*-C_6H_4-Alk** compounds we denote by symbol “**N**j”. Number **N** (N = 1–26) is given by bold and determines a row of compounds **containing the same substituent "Y".** Letter "j" denotes the **type of alkyl substituent** Alk: j = a-d.



1-26

where Y = NMe_2 (**1**), NH_2 (**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**), NO_2 (**16**), OAc (**17**), CH_2Cl (**18**), CH_2Br (**19**), EtC=O (**20**), SO_2Cl (**21**), F (**22**), Cl (**23**), I (**24**), CN (**25**), COOEt (**26**).

Unfortunately, because of the insufficient amount of spectral data for the compounds of "A" type in the informational sources (see about them below) we were able to construct only 10 complete four-termed rows (**Na-Nd)** for compounds **4-Y-C_6H_4-Alk**. "Y" substituents in them are: NH_2 (compounds **2a-2d**), **OH** (**3a-3d**), **OMe** (**4a-4d**), **Me** (**5a-5d**), **Ph** (**9a-9d**), **H** (**10a-10d**), **COOH** (**12a-12d**), **CH=O** (**15a-15d**), **NO_2** (**16a-16d**), **OAc** (**17a-17d**). For 16 substituents we constructed incomplete rows, where Y: NMe_2 (**1**), Et (**6**), Pr^i (**7**), Bu^t (**8**), Br (**11**), COOMe (**13**), Ac (**14**), CH_2Cl (**18**), CH_2Br (**19**), EtC=O (**20**), SO_2Cl (**21**), F (**22**), Cl (**23**), I (**24**), CN (**25**), COOEt (**26**).

The compounds of "B" type are discussed below.

II. Experimental data

II.1. Basic spectral parameters $\delta_i^{C,Nj}$

Introduced symbols and informational sources. Basic spectral parameters in NMR ^{13}C spectra of para-disubstituted benzenes are denoted generally by symbols $\delta_i^{C,Nj}$. The superscript means: a) spectrum type ("C" - carbon); b) number of compound (N); c) type of alkyl substituent "j". In the subscript the symbol "i" denotes the position of investigated carbon atom in the phenyl ring (i= *ipso-*, *o-*, *m-* or *p-*) or number f carbon atoms in phenyl ring. In some cases the superscript contains number of literature source in square brackets and subscript contains the type of compound: “α” for the compounds of A type and “β” – for the compounds of “B” type, e.g. $\delta_{ipso,\alpha}^{C,\mathbf{3d}[6]}$ or $\delta_{4,\alpha}^{C,\mathbf{10c}[7]}$.

The selection of spectral data sources is based on the consideration of their availability and compatibility, criteria of which were examined earlier in [5]. We used $\delta_i^{C,Nj}$ 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 δ^C values upon the solvent nature [8]. Comparing the small changes in the values of basic spectral parameters $\delta_i^{C,Nj}$ as a result of possible spatial interaction between molecule fragments, it is actually impossible to take into account greater changes of spectral parameter $\Delta\delta_{i,solv.}^{C,Nj}$, which may be caused by different nature of the solvents. Therefore, in this paper we did not discussed spectra obtained in other solvents (for example, DMSO-d_6).

II.1.2. Signals attribution in NMR ^{13}C spectra

The chemical shifts values of singlet signals are given with the accuracy of 0.01 ppm for every type of carbon nuclei $\delta_i^{C,Nj}$ of phenyl ring. Spectra NMR ^{13}C were obtained using complete suppression method of spin-spin interaction {^{1}H -^{13}C} and given in [6] and [7]. The average possible error for the determination of $\delta_i^{C,Nj}$ parameters is estimated as 0.10 ppm. The frequency of instruments by means of which spectra were recorded is not such significant as for spectra NMR ^{1}H, thus we do not discussed it here.

The author’s attribution of signals which is absent in [7] we fulfilled by ourselves. One of two intensive peaks in the spectral region of 124–131 ppm we attribute to the absorption of two carbon atoms of phenyl ring - atoms (C-2 and C-6), which are located in *ortho*-position concerning the alkyl substituent Alk. The other intensive peak is caused by the absorption of *meta*-carbon atoms C-3 and C-5 and situated within wider region (112–132 ppm). The same as in a case of NMR ^{1}H spectra, if values of $\delta_2^{C,Nj}$ and $\delta_3^{C,Nj}$ differ by the value less than 0.5 ppm, the unambiguous attribution of both signals may be difficult[i]. In such a case they may be exchange in accordance with [6].

Two less intensive signals remained in the region of 90–165 ppm are specified by the absorption of nuclei of *para*-carbon atom C-4 (which substituent Y is attached to) and *ipso*-carbon atom (which alkyl substituent Alk is attached to). Our attribution of all 4 aryl signals in the spectra given in [7] we correlated with author’s attribution of signals in spectra given in [6].

All data of NMR ^{13}C spectra are represented in Tables 1-5. The tables’ structure and symbols are the same those given in [1] for NMR ^{1}H spectra. Every cell of the tables where values of basic spectral parameter $\delta_i^{C,\mathbf{N}j}$ are present, contain two digits in column. The upper part of column contain parameter $\delta_i^{C,\mathbf{N}j[7]}$ taken from [7] and typed by usual; the bottom part contain the same parameter $\delta_i^{C,\mathbf{N}j[6]}$ taken from [6] and typed by bold. If the parameter is absent, we put dash.

For tert-butyl compounds (Y-C_6H_4-Bu^t) with numbers **N**d we used additional spectral data $\delta_i^{C,\mathbf{N}d[9]}$, taken from [9]. In the original paper [9] values $\delta_i^{C,\mathbf{N}d[9]}$ are given with the accuracy of 0.1 ppm. Almost all parameters $\delta_i^{C,\mathbf{N}d[9]}$ are in a agreement [5] with the same values $\delta_i^{C,\mathbf{N}d[7]}$ and $\delta_i^{C,\mathbf{N}d[6]}$. However, we consider parameter $\delta_i^{C,\mathbf{N}d[9]}$ as least reliable among all 3 data of $\delta_i^{C,\mathbf{N}d}$.

Table 1 represents the basic spectral parameters $\delta_i^{C,\mathbf{N}a}$ only for para-methylsubstituted benzenes **4-Y-C_6H_4-Me** (**1a-26a**). For other types of substituents (**1j-26j**, where: j = b,c,d) the differential parameters $\Delta\delta_i^{C,\mathbf{N}j}$ are given in corresponding cells instead of basic spectral parameters $\delta_i^{C,\mathbf{N}j}$.

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

The differential spectral parameters $\Delta\delta_i^{C,Nj}$ were calculated using formula (1), the same as in [1]:

$$\Delta\delta_i^{C,\mathbf{N}j} = \delta_i^{C,\mathbf{N}j(n)} - \delta_i^{C,\mathbf{N}a(0)} \qquad (1)$$

where $\delta_i^{C,\mathbf{N}j(n)}$ (j = b,c,d) is a basic spectral parameter in those para-disubstituted benzenes, in which substituent “Alk” is not a methyl group (n ≠ 0, Alk ≠ Me), i.e. $\delta_i^{C,\mathbf{N}j\,(n)} \neq \delta_i^{C,\mathbf{N}a(0)}$.

Structure of Table 1. The first of four columns contains the values of basic spectral parameter ($\delta_i^{C,\mathbf{N}a(0)}$). Next three columns contain calculated differential spectral parameters $\Delta\delta_i^{C,\mathbf{N}j}$ for compounds **1j-26j.** The sign of differential parameter (“+” or “-“) is obligatory, including positive values. The values of basic spectral parameters $\delta_i^{C,\mathbf{N}j}$ for compounds **1j-26j** (where j = b,c,d) are absent in Table 1. They may be calculated by adding of corresponding differential parameter with basic spectral parameter $\delta_i^{C,\mathbf{N}a}$**.**

Every cell of differential spectral parameters $\Delta\delta_i^{C,\mathbf{N}j}$ (the same as for basic parameter $\delta_i^{C,\mathbf{N}j}$) contain column consisting of two or three (for parameters $\Delta\delta_i^{C,\mathbf{N}d[9]}$) values. The upper value is calculated by formula (1): $\Delta\delta_i^{C,\mathbf{N}j[7]} = \delta_i^{C,\mathbf{N}j[7]} - \delta_i^{C,\mathbf{N}a[7]}$, using only basic parameters $\delta_i^{H,\mathbf{N}j[7]}$ taken from [7]. The bottom value (in cases when j≠d) is the same calculated parameter $\Delta\delta_i^{C,\mathbf{N}j[6]}$, using only parameters $\delta_i^{H,\mathbf{N}j[6]}$ taken from [6]. The upper digit is usual, the bottom one is bold; both digits are without brackets. Such parameters we call “non-crossed” (see below).

In those cases when the value of basic spectral parameter $\delta_i^{C,Nj}$ is absent in Refs. [6] or [7], it is impossible to calculate the value of corresponding “non-crossed” 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 data given in Refs. [6] and [7] and placed in the cell instead of absent “non-crossed” value. “Crossed” differential parameters are marked by bold in parentheses. For example, “crossed’ parameter may be calculated by formula: $(\boldsymbol{\Delta\delta_o^{C,Nj}}) = \delta_o^{C,Nj[7]} - \delta_o^{C,Na[6]}$, or on the contrary: $(\boldsymbol{\Delta\delta_o^{C,Nj}}) = \delta_o^{C,Nj[6]} - \delta_o^{C,Na[7]}$.

For some tert-butyl compounds (Y-C$_6$H$_4$-Bu^t) **Nd (**in those cases when values of basic spectral parameters $\delta_i^{C,Nj[9]}$ are present in [9]) the value of “crossed” differential parameter $\Delta\delta_i^{C,\mathbf{Nd}[9]}$ is given as third value in the column of corresponding cells. The values are typed by bold in parentheses. Usually they are calculated by formula: $\Delta\delta_i^{C,\mathbf{Nd}[9]} = \delta_i^{C,\mathbf{Nd}[9]} - \delta_i^{C,Na[7]}$ (in those cases when we have $\delta_i^{C,Na[7]}$ value). For the compounds **3** and **25** the value $\delta_i^{C,Na[7]}$ is absent. That is why we calculated “crossed” parameter as: $\Delta\delta_i^{C,\mathbf{Nd}[9]} = \delta_i^{C,\mathbf{Nd}[9]} - \delta_i^{C,Na[6]}$.

Table 1

Values of basic ($\delta_i^{C,Na}$) and differential ($\Delta\delta_i^{C,Nj}$) spectral parameters of compounds **1-26** (atoms C-2 and C-3).

Number of row	Substituent Y	Parameters of nuclei of *ortho*-carbon atoms				Parameters of nuclei of *meta*-carbon atoms			
		$\delta_2^{C,\mathbf{Na}}$	$\Delta\delta_2^{C,\mathbf{N}b}$	$\Delta\delta_2^{C,\mathbf{N}c}$	$\Delta\delta_2^{C,\mathbf{N}d}$	$\delta_3^{C,\mathbf{Na}}$	$\Delta\delta_3^{C,\mathbf{N}b}$	$\Delta\delta_3^{C,\mathbf{N}c}$	$\Delta\delta_3^{C,\mathbf{Nd}}$
1	NMe$_2$	129.53 **129.57** -	-	-	-3.75 **-3.78** ***(-3.73)***	113.14 **113.20** -	-	-	-0.58 **-0.55** ***(-0.34)***
2	NH$_2$	129.68 **129.76** -	-1.15 **-1.19** -	-2.63 **-2.65** -	-3.72 **-3.77** ***(-3.78)***	115.18 **115.28** -	+0.05 **+0.03** -	-0.05 **-0.07** -	-0.35 **-0.37** ***(-0.28)***
3	OH	- **130.17** -	**(-1.27)** **-1.19** -	**(-2.73)** **-2.65** -	**(-3.76)** **-3.70** ***(-3.67)***	- **115.35** -	**(-0.15)** **+0.04** -	**(-0.25)** **-0.04** -	**(-0.59)** **-0.39** ***(-0.35)***
4	OMe	129.84 **129.94** -	**(-1.09)** **-1.19** -	**(-2.59)** **-2.69** -	**(-3.71)** **-3.81** ***(-3.64)***	113.69 **113.81** -	**(+0.14)** **+0.02** -	**(+0.21)** **+0.09** -	**(-0.32)** **-0.44** ***(-0.31)***
5	Me	128.90 **128.97** -	-1.18 **-1.19** -	-2.65 **-2.66** -	-3.80 **-3.84** ***(-3.80)***	128.90 **128.97** -	+0.08 **+0.08** -	+0.05 **+0.08** -	-0.20 **-0.21** ***(-0.10)***
6	Et	128.98 **129.05**	-1.21 **-1.21**	-	-	127.72 **127.72**	+0.05 **+0.12**	-	-
7	Pr^i	128.95 **129.05**	-	-2.69 **-2.71**	-	126.25 **126.34**	-	+0.01 **+0.03**	-

8	Bu^t	128.70 **128.76** -	-	-	-3.86 **-3.88** ***(-3.90)***	125.10 **125.13** -	-	-	-0.26 **-0.25** ***(-0.30)***
9	Ph	129.43 **129.45** -	-1.21 **-1.19** -	-2.65 **-2.67** -	**(-3.74)** **-3.76** ***(-3.73)***	126.93 **126.92** -	+0.01 **+0.06** -	+0.03 **+0.03** -	**(-0.15)** **-0.14** ***(+0.07)***
10	H	129.01 **129.09** -	-1.18 **-1.20** -	-2.63 **-2.67** -	-3.83 **-3.93** ***(-3.81)***	128.22 **128.28** -	+0.06 **+0.07** -	+0.05 **+0.06** -	-0.21 **-0.26** ***(-0.12)***
11	Br	130.76 **130.78** -	-1.18 **-1.17** -	-	-3.64 **-3.65** ***(-3.66)***	131.21 **131.23** -	+0.07 **+0.10** -	-	-0.22 **-0.24** ***(-0.30)***
12	COOH	129.19 - -	- **(-1.15)** -	-2.60 **(-2.54)** -	- **(-3.73)** ***(-3.69)***	130.24 - -	- **(+0.16)** -	+0.15 **(+0.26)** -	- **(-0.06)** ***(-0.04)***
13	COOMe	129.04 **129.09**	-	-	-3.76 **-3.77**	129.58 **129.62**	-	-	-0.18 **-0.17**
14	Ac	129.21 **129.23** -	-1.18 **-1.16** -	-	- - ***(-3.71)***	128.40 **128.43 -**	+0.01 **+0.06** -	-	- - ***(-0.13)***
15	CH=O	128.68 **129.70**	-1.17 **-1.16**	-2.59 **-2.58**	**(-3.72)** **-3.74**	129.79 **129.76**	+0.13 **+0.19**	+0.16 **+0.21**	**(-0.12)** **-0.09**
16	NO_2	129.79 **129.82** -	-1.17 **-1.10** -	-2.52 **-2.52** -	- - ***(-3.49)***	123.46 **123.51** -	+0.13 **+0.10** -	+0.18 **+0.16** -	- - ***(-0.16)***
17	$OCOCH_3$	129.87 **129.91** -	**(-1.14)** **-1.18** -	**(-2.59)** **-2.63** -	**(-3.60)** **-3.64** ***(-3.57)***	121.20 **121.27** -	**(+0.09)** **+0.02** -	**(+0.07)** **0.00** -	**(-0.33)** **-0.40** ***(-1.20)***
18	CH_2Cl	129.37 **129.40**	-	-	-3.74 **-3.71**	128.53 **128.56**	-	-	-0.23 **-0.22**
19	CH_2Br	129.43 **129.43**	-	-	-3.75 **-3.79**	128.92 **128.94**	-	-	-0.22 **-0.24**
20	EtCO	129.19 -	- **(-1.14)**	-	- **(-3.72)**	128.06 -	- **(+0.16)**	-	- **(-0.09)**
21	SO_2Cl	130.23 **130.28**	**(-1.05)** **-1.10**	-	-3.55 **-3.58**	126.99 **127.02**	**(+.15)** **+0.12**	-	-0.15 **-0.10**
22	F	130.29 **130.39** -	-	-	- - ***(-3.49)***	114.92 **114.99** -	-	-	- - ***(-0.22)***
23	Cl	130.32 - -	-	-	- - ***(-3.52)***	128.24 - -	-	-	- - ***(-0.04)***
24	I	131.13 **131.11** -	-	-	- - ***(-3.63)***	137.20 **137.14** -	-	-	- - ***(-0.10)***
25	CN	- **129.92** -	-	-	- **-3.76** ***(-3.71)***	- **131.99** -	-	-	- **-0.02** ***(+0.01)***
26	CO_2Et	129.00 **129.04** -	-	-	- - ***(-3.70)***	129.53 **129.63** -	-	-	- - ***(-0.03)***

Compounds **1-26** (atoms C-1 and C-4)									
Number of row	Substituent Y	Parameters of nuclei of *ipso*-carbon atoms				Parameters of nuclei of *para*-carbon atoms			
		$\delta_1^{\mathrm{C,N}}$[a]	$\Delta\delta_1^{\mathrm{C,N}}$[b]	$\Delta\delta_1^{\mathrm{C,N}}$[c]	$\Delta\delta_1^{\mathrm{C,N}}$[d]	$\delta_4^{\mathrm{C,N}}$[a]	$\Delta\delta_4^{\mathrm{C,N}}$[b]	$\Delta\delta_4^{\mathrm{C,N}}$[c]	$\Delta\delta_4^{\mathrm{C,N}}$[d]
1	NMe_2	125.97 **125.96** **-**	-	-	+13.33 **+13.37** ***(+13.53)***	148.78 **148.83** **-**	-	-	-0.28 **-0.26** ***(-0.34)***
2	NH_2	127.60 **127.61** **-**	+6.72 **+6.75** **-**	+11.41 **+11.43** **-**	+13.62 **+13.70** ***(+13.60)***	143.81 **143.98** **-**	+0.26 **+0.17** **-**	+0.29 **+0.25** **-**	-0.06 **-0.15** ***(-0.28)***
3	OH	- **130.17** **-**	**(+6.48)** **+6.59** **-**	**(+11.10)** **+11.24** **-**	**(+13.38)** **+13.51** ***(+13.53)***	- **152.92** **-**	**(+0.19)** **+0.13** **-**	**(+0.27)** **+0.13** **-**	**(-0.02)** **-0.18** ***(-0.35)***
4	OMe	129.76 **129.94** **-**	**(+6.62)** **+6.44** **-**	**(+11.35)** **+11.17** **-**	**(+13.46)** **+13.28** ***(+13.53)***	157.50 **157.65** **-**	**(+0.32)** **+0.17** **-**	**(+0.40)** **+0.25** **-**	**(-0.17)** **-0.32** ***(-0.31)***
5	Me	134.62 **134.66** **-**	+6.56 **+6.56** **-**	+11.23 **+11.23** **-**	+13.46 **+13.45** ***(+13.58)***	134.62 **134.66** **-**	+0.31 **+0.30** **-**	+0.47 **+0.45** **-**	+0.12 **+0.07** ***(-0.10)***
6	Et	134.93 **134.96**	+6.49 **+6.49**	-	-	141.18 **141.22**	+0.24 **+0.23**	-	-
7	Pr^i	135.09 **135.11**	-	+11.04 **+11.08**	-	145.85 **145.89**	-	+0.28 **+0.30**	-
8	Bu^t	134.74 **134.73** **-**	-	-	+13.20 **+13.27** ***(+13.06)***	148.08 **148.11** **-**	-	-	-0.14 **-0.11** ***(-0.30)***
9	Ph	136.92 **136.86** **-**	+6.37 **+6.48** **-**	+10.98 **+10.99** **-**	**(+13.30)** **+13.36** ***(+13.38)***	138.33 **138.70** **-**	+0.24 **+0.22** **-**	+0.37 **+0.35** **-**	**(0.00)** **-0.02** ***(+0.07)***
10	H	137.81 **137.83** -	+6.39 **+6.41** -	+11.00 **+11.00** **-**	+13.22 **+13.16** ***(+13.19)***	125.29 **125.38** -	+0.28 **+0.27** **-**	+0.44 **+0.41** **-**	+0.08 **-0.01** ***(-0.12)***
11	Br	136.70 **136.70** **-**	+6.37 **+6.39** -	-	+13.34 **+13.31** ***(+13.30)***	119.03 **119.08** **-**	+0.21 **+0.21** **-**	-	+0.13 **+0.09** ***(-0.30)***
12	COOH	144.62 **-** **-**	**-** **(+6.19)** **-**	+10.71 **(+10.80)** **-**	- **(+12.96)** ***(+12.98)***	126.80 **-** **-**	- **(+0.10)** **-**	+0.03 **(+0.14)** **-**	- **(-0.10)** ***(0.00)***
13	COOMe	143.51 **143.51**	-	-	+12.95 **+13.03**	127.43 **127.54**	-	-	-0.08 **-0.12**

14	Ac	143.76 **143.74** **-**	+6.20 **+6.21** **-**	-	- **-** ***(+13.04)***	134.79 **134.79** **-**	+0.21 **+0.30** **-**	-	- **-** ***(+0.11)***
15	CH=O	145.45 **145.43**	+6.17 **+6.21**	+10.70 **+10.72**	**(+12.94)** **+12.96**	134.29 **134.29**	+0.09 **+0.22**	+0.22 **+0.33**	**(-0.11)** **-0.11**
16	NO_2	145.96 **145.95** **-**	**(+6.23)** **+6.24** **-**	+10.61 **+10.66** **-**	- **-** ***(+12.94)***	146.13 **146.31** **-**	**(+0.16)** **-0.02** **-**	+0.18 **+0.16** **-**	- **-** ***(-0.03)***
17	$OCOCH_3$	135.35 **135.36** **-**	**(+6.35)** **+6.34** **-**	**(+10.93)** **+10.92** **-**	**(+13.18)** **+13.17** ***(+13.25)***	148.47 **148.61** **-**	**(+0.18)** **+0.04** **-**	**(+0.40)** **+0.26** **-**	**(-0.09)** **-0.23** ***(-0.22)***
18	CH_2Cl	138.23 **138.24**	-	-	+13.22 **+13.26**	134.56 **134.61**	-	-	-0.06 **-0.07**
19	CH_2Br	138.30 **138.24**	-	-	+13.18 **+13.11**	134.82 **134.85**	-	-	-0.10 **-0.16**
20	EtCO	143.52 **-**	- **(+6.24)**	-	+12.98 **-**	134.43 **-**	- **(+0.28)**	-	+0.07 **-**
21	SO_2Cl	146.84 **146.93**	**(+6.13)** **+6.04**	-	+12.81 **+12.74**	141.60 **141.70**	**(+.22)** **+0.12**	-	-0.12 **-0.07**
22	F	133.35 **133.42** **-**			- **-** ***(+13.38)***	161.13 **161.24** **-**			- **-** ***(-0.24)***
23	Cl	136.18 **-** **-**			- **-** ***(+13.42)***	131.07 **-** **-**			- **-** ***(-0.04)***
24	I	137.29 **137.36** **-**			- **-** ***(+13.51)***	90.20 **90.14** **-**			- **-** ***(+0.40)***
25	CN	- **143.75** **-**			- **+12.95** ***(+12.90)***	- **109.41** **-**			- **-0.05** ***(+0.09)***
26	CO_2Et	143.51 **143.35** **-**			- **-** ***(+12.89)***	127.99 **127.99** **-**			- **-** ***(-0.09)***

II.3. 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 or one more $\text{-}C^{\beta}R^1R^2R^3$ group. 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 **1-26** of "B" type have three[ii] 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 constructed 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»). In [6, 7] spectral data are absent for the compounds with alkyl substituents containing two methyl groups ($R^1 = R^2 = CH_3$, $R^3 = H$, n=2), i.e. for the third term, or three methyl groups, i.e. for the fourth term of complete row.

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 were 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.3.1. Structure of Tables 2-5

Tables 2-5 represent values of differential spectral parameters ($\Delta\delta_i^{C,\mathbf{N}j}$) calculated by formula (2) similar to the formula (1):

$$\Delta\delta_i^{C,\mathbf{N}j} = \delta_i^{C,\mathbf{N}jn} - \delta_i^{C,\mathbf{Nj1}}$$

(2)

The minuend $\delta_i^{C,\mathbf{N}jn}$ (where: j_n = e ÷ k, see above) is a basic parameter of the corresponding “non-first” compound of the row denoted as “j_n”. The subtrahend is a basic spectral $\delta_i^{C,\mathbf{Nj1}}$ (where: j_1 = b, c, d), which is the first in the investigated row.

The structure of Table 2 is similar to that of Table 2 in [1]. The values of basic ($\delta_2^{C,\mathbf{Nj1}}$) and calculated differential ($\Delta\delta_2^{C,\mathbf{N}j}$) parameters for *ortho*-carbon atoms of phenyl ring are represented for the compounds **2-17** of “B” type with alkyl groups e,f,g,h and k. The symbols, cells structure and font type are the same as in Table 1. The first three columns contain values of corresponding basic parameters and five next columns – calculated values of differential parameters: e (e-b), f (f-b), g (g-b), h (h-c) and k (k-d). The structure of Tables 3-5 (for *meta*-, *para*- and *ipso*-carbon atoms of phenyl ring) is the same.

Table 2

Values of basic ($\delta_o^{C,Nj1}$) and differential ($\Delta\delta_o^{C,Nj}$) spectral parameters of ortho-carbon atoms in the compounds **2-17** of “B” type (Alk = $-C^{\alpha}Z^1Z^2-C^{\beta}R^1R^2R^3$)

Number of row	Substituent Y	Basic spectral parameters of carbon atoms of the first term of the row			Differential spectral parameters of carbon atoms of the second-fourth terms of the row				
		$\delta_o^{C,\mathbf{N}b}$	$\delta_o^{C,\mathbf{N}c}$	$\delta_o^{C,\mathbf{N}d}$	$\Delta\delta_o^{C,Ne}$ (e-b)	$\Delta\delta_o^{C,N}$ f (f-b)	$\Delta\delta_o^{C,Ng}$ (g-b)	$\Delta\delta_o^{C,Nh}$ (h-c)	$\Delta\delta_o^{C,Nk}$ (k-d)
2	NH_2	128.53 **128.47**	127.05 **127.11**	-	+0.67 **+0.57**	-	-	+0.67 **(+0.61)**	-
3	OH	128.90 **128.98**	127.44 **127.52**	126.41 126.47	+0.60 **+0.61**	-	-	**(+0.69)** **+0.61**	+0.69 **+0.66**
4	OMe	-	- **127.25**	**-**	**-**	**-**	**-**	**-** **+0.63**	**-**
5	Me	127.72 **127.78**	**-**	**-**	**(+0.66)** **+0.60**	-	-	**-**	**-**
10	H	127.83 **127.89**	126.38 **126.42**	125.18 **125.16**	+0.62 **+0.62**	**(+1.30)** **+1.24**	+2.59 +**2.56**	+0.64 **+0.65**	**(+0.74)** **+0.76**
11	Br	129.58 **129.61**	-	-	+0.58 **+0.58**	-	-	-	-
12	COOH	- **128.04**	-	-	**(+0.55)** **+0.57**	-	-	-	-
14	Ac	128.03 **128.07**	-	-	**(+0.64)** **+0.60**	(+1.25) +1.21	-	-	-
15	CH=O	128.51 **128.54**	-	-	**-**	(+1.23) +1.20	-	-	-
16	NO_2	-	127.27 **127.30**	-	-	**-**	-	**(+0.59)** **+0.56**	-
17	OAc	-	- **127.28**	-	-	**-**	-	**-** **+0.59**	-

Table 3

Values of basic ($\delta_m^{C,Nj1}$) and differential ($\Delta\delta_m^{C,Nj}$) spectral parameters of *meta*-carbon atoms in the compounds **2-17** of “B” type (Alk = $-C^{\alpha}Z^1Z^2-C^{\beta}R^1R^2R^3$)

Number of row	Substituent Y	Basic spectral parameters of carbon atoms of the first term of the row			Differential spectral parameters of carbon atoms of the second-fourth terms of the row				
		$\delta_m^{C,\mathbf{N}b}$	$\delta_m^{C,\mathbf{N}c}$	$\delta_m^{C,\mathbf{N}d}$	$\Delta\delta_m^{C,N}$ e (e-b)	$\Delta\delta_m^{C,}$ Nf (f-b)	$\Delta\delta_m^{C,N}$ g (g-b)	$\Delta\delta_m^{C,N}$ h (h-c)	$\Delta\delta_m^{C,N}$ k (k-d)
2	NH_2	115.23 **115.31**	115.13 **115.21**	-	-0.10 **-0.05**	-	-	+0.04 **(-0.04)**	-
3	OH	115.20 **115.39**	115.10 **115.31**	114.76 114.96	-0.11 **-0.10**	-	-	**(+0.19)** **-0.02**	+0.03 **-0.03**
4	OMe	-	- **113.90**	**-**	**-**	**-**	**-**	**-** **-0.10**	**-**
5	Me	128.98 **129.05**	**-**	**-**	**(-0.03)** **-0.10**	-	-	**-**	**-**
10	H	128.28 **128.35**	128.27 **128.34**	128.01 **128.02**	-0.09 **-0.09**	(-0.18) **-0.25**	-0.70 **-0.77**	-0.07 **-0.06**	(-0.02) **-0.03**

11	Br	131.28 **131.33**	-	-	-0.10 **-0.09**	-	-	-	-
12	COOH	- **130.40**	-	-	**(-0.14)** **-0.06**	-	-	-	-
14	Ac	128.51 **128.58**	-	-	**(-0.04)** **-0.11**	**(-0.19)** **-0.30**	-	-	-
15	CH=O	129.92 **129.95**	-	-	**-**	**(-0.18)** **-0.21**	-	-	-
16	NO_2	-	123.64 **123.67**	-	-	-	-	**(0.00)** **-0.03**	-
17	OAc	-	- **121.27**	-	-	-	-	**-** **-0.05**	-

Table 4

Values of basic ($\delta_1^{C,Nj}$) and differential ($\Delta\delta_1^{C,Nj}$) spectral parameters of *ipso*-carbon atoms in the compounds **2-17** of “B” type (Alk = $-C^{\alpha}Z^1Z^2-C^{\beta}R^1R^2R^3$)

Number of row	Substituent Y	Basic spectral parameters of carbon atoms of the first term of the row			Differential spectral parameters of carbon atoms of the second-fourth terms of the row				
		$\delta_1^{C,Nb}$	$\delta_1^{C,Nc}$	$\delta_1^{C,Nd}$	$\Delta\ \delta_1^{C,Ne}$ (e-b)	$\Delta\ \delta_1^{C,Nf}$ (f-b)	$\Delta\ \delta_1^{C,Ng}$ (g-b)	$\Delta\ \delta_1^{C,Nh}$ (h-c)	$\Delta\ \delta_1^{C,Nk}$ (k-d)
2	NH_2	134.32 **134.36**	139.01 **139.04**	-	-1.57 **-1.59**	-	-	-1.18 **(-1.21)**	-
3	OH	136.65 **136.76**	141.27 **141.41**	143.55 143.68	-1.60 **-1.60**	-	-	-1.09 **(-1.23)**	-1.68 **-1.73**
4	OMe	-	- **141.11**	**-**	**-**	**-**	-	**-** **-1.27**	**-**
5	Me	141.18 **141.22**	-	-	**(-1.58)** **-1.62**	-	-	-	-
10	H	144.20 **144.24**	148.81 **148.83**	151.03 **150.99**	-1.55 **-1.57**	**(-2.56)** **-2.60**	-4.53 **-4.54**	-1.18 **-1.18**	**(-1.62)** **-1.58**
11	Br	143.07 **143.09**	-	-	-1.57 **-1.58**	-	-	-	-
12	COOH	- **150.81**	-	-	**(-1.51)** **-1.51**	-	-	-	-
14	Ac	149.96 **149.95**	-	-	**(-1.51)** **-1.50**	**(-2.47)** **-2.46**	-	-	-
15	CH=O	151.62 **151.64**	-	-	**-**	**(-2.38)** **-2.40**	-	-	-
16	NO_2	-	156.57 **156.61**	-	-	-	-	**(-1.03)** **-1.07**	-
17	OAc	-	- **146.28**	-	-	-	-	**-** **-1.16**	-

Table 5

Values of basic ($\delta_4^{C,Nj}$) and differential ($\Delta\delta_4^{C,Nj}$) spectral parameters of *para*-carbon atoms in the compounds **2-17** of “B” type (Alk = $-C^{\alpha}Z^{1}Z^{2}-C^{\beta}R^{1}R^{2}R^{3}$)

Number of row	Substituent Y	Basic spectral parameters of carbon atoms of the first term of the row			Differential spectral parameters of carbon atoms of the second-fourth terms of the row				
		$\delta_4^{C,Nb}$	$\delta_4^{C,Nc}$	$\delta_4^{C,Nd}$	$\Delta\ \delta_4^{C,Ne}$ (e-b)	$\Delta\ \delta_4^{C,Nf}$ (f-b)	$\Delta\ \delta_4^{C,Ng}$ (g-b)	$\Delta\ \delta_4^{C,Nh}$ (h-c)	$\Delta\ \delta_4^{C,Nk}$ (k-d)
2	NH_2	144.07 **144.15**	144.10 **144.23**	-	-0.02 **+0.08**	-	-	+0.04 **(-0.09)**	-
3	OH	153.11 **153.05**	153.19 **153.05**	152.90 **152.74**	+0.04 **+0.04**	-	-	+0.04 **(+0.18)**	-0.03 **+0.03**
4	OMe	-	- **157.90**	-	-	-	-	- **0.00**	-
5	Me	134.93 **134.96**	-	-	**(+0.02)** **-0.01**	-	-	-	-
10	H	125.57 **125.65**	125.73 **125.79**	151.03 **150.99**	+0.01 **+0.02**	**(+0.10)** **+0.02**	+0.09 **+0.06**	**0.00** **+0.03**	**(-0.04)** **-0.04**
11	Br	119.24 **119.29**	-	-	+0.02 **+0.05**	-	-	-	-
12	COOH	- **126.90**	-	-	**(-0.07);** **+0.14**	-	-	-	-
14	Ac	135.00 **135.09**	-	-	**(+0.08)** **-0.01**	**(+0.07)** **-0.02**	-	-	-
15	CH=O	134.38 **134.51**	-	-	-	**(+0.09)** **-0.04**	-	-	-
16	NO_2	-	146.24 **146.36**	-	-	-	-	**(+0.14)** **+0.02**	-
17	OAc	-	- **148.87**	-	-	-	-	- **+0.07**	-

III. Results and Discussion

According to the reasons stated in [1] we consider parameters $\delta_i^{C,Nj[7]}$ the most reliable. Therefore, while comparing differential parameters $\Delta\delta_i^{C,Nj}$ and discussing the results we prefer “non-crossed” parameters $\Delta\delta_i^{C,Nj[7]}$, not $\Delta\delta_o^{C,N(i)[6]}$. We reckon that accuracy and reliability of both “non-crossed” differential parameters $\Delta\delta_i^{C,Nj\ [7]}$ and $\Delta\delta_i^{C,Nj[6]}$ are higher than accuracy of “crossed” parameters **($\Delta\delta_i^{H,Nj}$).** To our mind, the valuable of “crossed” parameters is lower compared with “non-crossed” ones, especially of $\Delta\delta_i^{C,Nd[9]}$ parameters. The main task of “crossed” parameter is to confirm the value of existed “non-crossed” $\Delta\delta_i^{H,Nj[7]}$ or $\Delta\delta_i^{H,Nj[6]}$; in other case the values of “crossed” differential parameters are not taken into consideration. By above-mentioned reasons the the “crossed” parameters $\Delta\delta_i^{C,\mathbf{N}d[9]}$ are the least reliable.

III.1. Averaged (“mean”) values of differential parameters

For the analysis of dependence (see Tables 1-5) of differential parameters $\Delta\delta_{i,,\alpha}^{C,\mathbf{N}j}$ and $\Delta\delta_{i,,\beta}^{C,\mathbf{N}j}$ upon the position and numbers of branching in alkyl substituent Alk it is advisable to use **arithmetic mean value** of every **differential parameter**. We call such parameters as “**mean parameters**”.

Symbols. **Mean differential parameters** in general we denote as “$\Delta\delta_i^j$”. The superscript of mean parameters does not contain spectrum type compared with individual parameters of particular compound ($\Delta\delta_i^{C,\mathbf{N}j}$, i.e. in our case “C” – carbon) and number of compounds (**N**). We denote only type of alkyl group “j”. After superscript letter there may be a digit which designates value n – number of methyl groups for substituents R^1, R^2, R^3. The subscript contain the symbol designating the position of carbon atoms in phenyl ring. A type of compound also may be shown (“α” or “β”), e.g. $\Delta\delta_{2,\alpha}^{c(2)}$ и $\Delta\delta_{м,\beta}^{e(1)}$.

Mean differential parameters calculated for the compounds **1-26** 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 four types depending upon the position of investigated carbon atom in phenyl ring. They may be united by general title “*ipso*-parameters”, “*ortho*-parameters”, *“meta*-parameters” or “*para*-parameters”. Then, for example, above-mentioned parameter $\Delta\delta_{2,\alpha}^{c(2)}$ belongs to the “*ortho*-α-type” and parameter $\Delta\delta_{m,\beta}^{e(1))}$ – to the parameters of “*meta*-β-type”.

III. 1.1. The value of mean parameters $\Delta\delta_i^j$

The value of every mean parameter $\Delta\delta_i^j$ is statistic by definition. To calculate mean parameters from the data of Tables 1-5 we used unequal amount of compounds, which is called as “number of examples”. The number of examples is given in the last column of Tables 6-9 (see below) in parentheses after mean value of corresponding parameter. For every compound we may calculate two individual parameters (and third individual parameter $\Delta\delta_i^{C,\mathbf{N}d[9]}$ in the case of some compounds **N**d). Therefore the **number of summands** for calculations of arithmetic average may be two or three times more than the number of examples. Maximum number of summands (51, see below) was used to calculate mean value of $\Delta\delta_1^d$ parameter.

Obviously, the higher numbers of examples is used for the calculations, the more reliable its "statistic validation". The greatest amount of spectral data $\Delta\delta^{N(i)}$ is for the compounds of "A" type, therefore we used the greatest number of examples (from 11 to 24) to calculate the mean parameters $\Delta\delta_{i,\alpha}^{j}$ and $\Delta\delta_{m,\alpha}^{j}$. For the calculation of $\Delta\delta_{i,\beta}^{,j}$ mean parameters the maximum number of available examples are significantly less (7).

Arbitrarily we admitted so minimum number of examples (5) which allows us to consider the calculated mean parameter as "statistically valid". Based on this criterion we consider all 12 α-parameters $\Delta\delta_{i,\alpha}^{j}$ for the compounds of "A" type as "statistically valid". At the same time we found only 8 "statistically valid" parameters for the compounds of "B" type: $\Delta\delta_{i,\beta}^{e}$ и $\Delta\delta_{i,\beta}^{h}$ (7 and 6 examples, relatively).

The rest 12 β-parameters are not "statistically valid". By the above-mentioned definition 4 parameters $\Delta\delta_{i,\beta}^{f}$ (by 3 examples) and $\Delta\delta_{i,\beta}^{k}$ (by 2 examples) are "statistically insufficiently valid". Anyway we consider them as well, taking into account this drawback. Four parameters $\Delta\delta_{i,\beta}^{g}$ cannot be considered as "mean parameters" because for their 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" ones and consider them 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 6-9. It is equal to five-fold accuracy (error of measurements), i.e. **0.50** ppm.

Structure of Tables 6-9. The results of calculations of mean differential parameters ($\Delta\delta_{i,}^{j}$) are given in the last column of every Table by bold and larger type with the accuracy of 0.01 ppm. The sign is obligatory ("+" or "-"). After the digit there are a number of examples used for the calculation of mean value in parentheses (as it was said above).

In the fourth (from the end) column there are intervals of values corresponding to the **"non-crossed" differential parameters** $\Delta\delta_{i}^{N(j)}$ taken from Tables 1-5 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 in Tables 6-9 regardless of font type used in Tables 1-5. After them the digit of compounds which determine the "boundary parameter" is given in parentheses by bold. We accepted that "crossed" parameters cannot be the "boundary parameters" because of their less reliability. Therefore if we calculate the mean parameter (for example $\Delta\delta_3^{d}$) the value of "crossed" parameter cannot be a summand (in the mentioned case it is $\Delta\delta_3^{C,17d[9]} = -1.20$ ppm). This value is lower than value of the least "non-crossed" parameter ($\Delta\delta_3^{C,\mathbf{2}d[7]} = -0.58$ ppm) which bounds the interval from the side of minimum values. The same situation is with the parameters from the side of maximum values. Therefore while calculations of some mean α-parameters the **number of examples** given in Tables 6-9 **is less than number of compounds** for which corresponding differential parameters (including "crossed" ones) were calculated.

The following two columns contain data concerning the **interval width** denoted by the symbol "$\Delta\Delta\delta_i^{j}$". The first column contains **absolute** values of interval width in ppm. We denote them as $\Delta\Delta\delta_{i,abs.}^{j}$. The second column has **relative** values of interval width in percents for **only "considerable" by absolute value mean parameters** (with some exception). We denote them as $\Delta\Delta\delta_{i,rel.}^{j}$. Parameter $\Delta\Delta\delta_{i,rel.}^{j}$ is calculated as quotient of interval width division by absolute value of "considerable" mean parameter, i.e. $\mathbf{\Delta\Delta\delta_{i,rel.}^{j} = \Delta\Delta\delta_{i,abs.}^{j} / |\Delta\delta_{i,}^{j}|}$. 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%.

The considerable number of intervals of "insignificant" mean parameters would be "wide" because of the small value of divisor comparable with dividend value. Therefore for some "insignificant" parameters the column "Relative width of interval" has dash in Tables 6-9.

Table 6

Mean values of calculated differential parameters $\Delta\delta_2^{j}$ for nuclei of *ortho*-carbon atoms in compounds **1-26**

Compound type (number of Table)	Alkyl group (its lettering in Tables 1-5	Value of "n" parameter	Minuend and subtrahend in formula: $\Delta\delta_2^{j} = \delta_2^{j} - \delta_2^{(0)}$	Mean parameter $\Delta\delta_2^{j}$, ppm				
				Symbol of mean parameter	Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**)	Absolute width of interval ($\Delta\Delta\delta_{2,\,abs.}^{j}$), ppm	Relative width of interval ($\Delta\Delta\delta_{2,rel.}^{j}$), %	Average value (number of examples in Tables 1 or 2 for calculations)

A (1)	Et (b)	1	b-a	$\Delta\delta_{2,\alpha}^{b}$	from (-1.10) (**16, 21**) to -1.21 (**6, 9, 10**)	0.11	9 (nar.)	**-1.17** (15)
A (1)	Pr^{i} (c)	2	c-a	$\Delta\delta_{2,\alpha}^{c}$	from -2.52 (**21**) to -2.71 (**7**)	0.19	7 (nar.)	**-2.62** (11)
A (1)	Bu^{t} (d)	3	d-a	$\Delta\delta_{2,\alpha}^{d}$	from -3.55 (**21**) to -3.93 (**10**)	0.38	10 (nar.)	**-3.73** (21)
B (2)	Pr (e)	1	e-b	$\Delta\delta_{2,\beta}^{e}$	from +0.57(**2**) to +0.67(**2**)	0.10	17 (nar.)	**+0.61** (7)
B (2)	Bu^{i} (f)	2	f-b	$\Delta\delta_{2,\beta}^{f}$	from +1.20 (**15**) to +1.30(**10**)	0.10	8 (nar.)	**+1.24** (3)
B (2)	Am^{neo} (g)	3	g-b	$\Delta\delta_{2,\beta}^{g}$	from +2.56 (**10**) to +2.59(**10**)	0.03	1 (nar.)	**+2.58** (1)
B (2)	Bu^{s} (h)	1	h-c	$\Delta\delta_{2,\beta}^{h}$	from +0.56 (**16**) to +0.67(**2**)	0.11	18 (nar.)	**+0.62** (6)
B (2)	Am^{t} (k)	3	k-d	$\Delta\delta_{2,\beta}^{k}$	from +0.66 (**3**) to +0.76 (**10**)	0.10	14 (nar.)	**+0.71** (2)

Table 7

Mean values of calculated differential parameters $\Delta\delta_3^{j}$ for nuclei of *meta*-carbon atoms in compounds **1-26**

Compound type (number of Table)	Alkyl group (its lettering in Tables 1-5	Value of "n" parameter	Minuend and subtrahend in formula: $\Delta\delta_3^{j} = \delta_3^{j} - \delta_3^{(0)}$	Mean parameter $\Delta\delta_3^{j}$, ppm				
				Symbol of mean parameter	Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**)	Absolute width of interval ($\Delta\Delta\delta_{3,\text{ abs.}}^{j}$), ppm	Relative width of interval ($\Delta\Delta\delta_{3,\text{rel.}}^{j}$), %	Average value (number of examples in Tables 1 or 2 for calculations)
A (1)	Et (b)	1	b-a	$\Delta\delta_{3,\alpha}^{b}$	from (+0.01) (**9, 14**) to +0.19 (**15**)	0.18	-	**+0.09** (14)
A (1)	Pr^{i} (c)	2	c-a	$\Delta\delta_{3,\alpha}^{c}$	from -0.07 (**2**) to +0.21 (**15**)	0.28	-	**+0.07** (11)
A (1)	Bu^{t} (d)	3	d-a	$\Delta\delta_{2,\alpha}^{d}$	from -0.58 (**1**) to -0.10	0.48	192 (wide)	**-0.25** (19)

					(**21**)			
B (2)	Pr (e)	1	e-b	$\Delta\delta_{3,\beta}^{e}$	from -0.11(**3, 14**) to -0.05(**2**)	0.06	67 (mid.)	**-0.09** (7)
B (2)	Bu^{i} (f)	2	f-b	$\Delta\delta_{3,\beta}^{f}$	from -0.30 (**14**) to -0.21(**15**)	0.09	36 (mid.)	**-0.25** (3)
B (2)	Am^{neo} (g)	3	g-b	$\Delta\delta_{3,\beta}^{g}$	from -0.77 (**10**) to -0.70(**10**)	0.07	9 (nar.)	**-0.74** (1)
B (2)	Bu^{s} (h)	1	h-c	$\Delta\delta_{3,\beta}^{h}$	from -0.10 (**4**) to +0.04(**2**)	0.14	-	**-0.04** (6)
B (2)	Am^{t} (k)	3	k-d	$\Delta\delta_{3,\beta}^{k}$	from -0.03 (**3, 10**) to +0.03 (**3**)	0.06	-	**-0.01** (2)

Table 8

Mean values of calculated differential parameters $\Delta\delta_1^{j}$ for nuclei of *ipso*-carbon atoms in compounds **1-26**

Compound type (number of Table)	Alkyl group (its lettering in Tables 1-5	Value of “n” parameter	Minuend and subtrahend in formula: $\Delta\delta_1^{j} = \delta_1^{j} - \delta_1^{(0)}$	Mean parameter $\Delta\delta_1^{j}$, ppm				
				Symbol of mean parameter	Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**)	Absolute width of interval ($\Delta\Delta\delta_{1,\ abs.}^{j}$), ppm	Relative width of interval ($\Delta\Delta\delta_{1,rel.}^{j}$), %	Average value (number of examples in Tables 1 or 2 for calculations)
A (1)	Et (b)	1	b-a	$\Delta\delta_{1,\alpha}^{b}$	from (+6.04) (**21**) to +6.75 (**2**)	0.71	11 (nar.)	**+6.38** (15)
A (1)	Pr^{i} (c)	2	c-a	$\Delta\delta_{1,\alpha}^{c}$	from +10.61 (**16**) to +11.43 (**2**)	0.82	7 (nar.)	**+11.01** (11)
A (1)	Bu^{t} (d)	3	d-a	$\Delta\delta_{1,\alpha}^{d}$	from +12.74 (**21**) to +13.70 (**2**)	0.96	7 (nar.)	**+13.24** (24)
B (2)	Pr (e)	1	e-b	$\Delta\delta_{1,\beta}^{e}$	from -1.62(**5**) to -1.50(**14**)	0.12	8 (nar.)	**-1.56** (7)
B (2)	Bu^{i} (f)	2	f-b	$\Delta\delta_{1,\beta}^{f}$	from -2.60 (**10**) to -2.40(**15**)	0.20	8 (nar.)	**-2.50** (3)
B (2)	Am^{neo} (g)	3	g-b	$\Delta\delta_{1,\beta}^{g}$	from -4.54 (**10**) to -4.53(**10**)	0.01	1 (nar.)	**-4.54** (1)

B (2)	Bu^s (h)	1	h-c	$\Delta\delta_{1,\beta}^{h}$	from -1.27 (**7**) to -1.07(**16**)	0.20	17 (nar.)	**-1.17** (6)
B (2)	Am^t (k)	3	k-d	$\Delta\delta_{1,\beta}^{k}$	from -1.73 (**3**) to -1.58 (**10**)	0,15	9 (nar.)	**-1.65** (2)

Table 9

Mean values of calculated differential parameters $\Delta\delta_4^j$ for nuclei of *para*-carbon atoms in compounds **1-26**

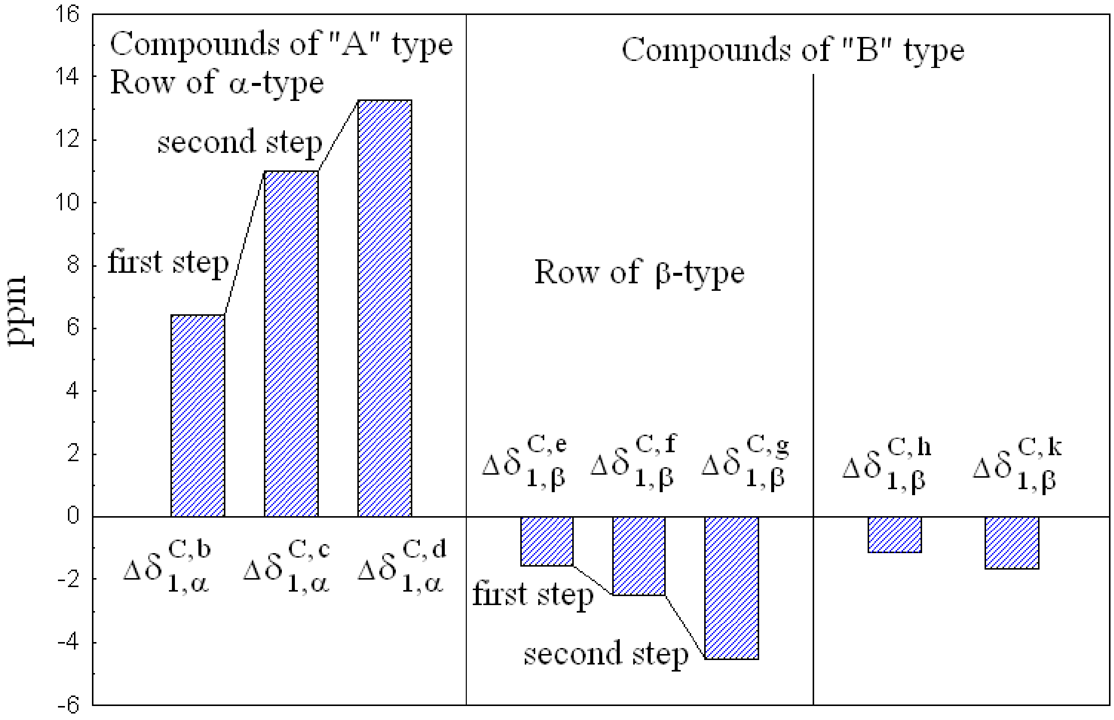
Compound type (number of Table)	Alkyl group (its lettering in Tables 1-5	Value of “n” parameter	Minuend and subtrahend in formula: $\Delta\delta_4^j = \delta_4^j - \delta_4^{(0)}$	Mean parameter $\Delta\delta_4^j$, ppm				
				Symbol of mean parameter	Interval of individual compounds parameters used for calculation of mean parameter (number of substituent **Y**)	Absolute width of interval ($\Delta\Delta\delta_{4,\ abs.}^{j}$), ppm	Relative width of interval ($\Delta\Delta\delta_{4,rel.}^{j}$), %	Average value (number of examples in Tables 1 or 2 for calculations)
A (1)	Et (b)	1	b-a	$\Delta\delta_{4,\alpha}^{b}$	from -0.02 (**16**) to +0.31 (**5**)	0.33	174 (wide)	**+0.19** (15)
A (1)	Pr^i (c)	2	c-a	$\Delta\delta_{4,\alpha}^{c}$	from +0.03 (**12**) to +0.47 (**5**)	0.44	151 (wide)	**+0.29** (11)
A (1)	Bu^t (d)	3	d-a	$\Delta\delta_{4,\alpha}^{d}$	from -0.32 (**4**) to +0.13 (**11**)	0.45	-	**-0.09** (23)
B (2)	Pr (e)	1	e-b	$\Delta\delta_{4,\beta}^{e}$	Non-calc.	-	-	**-**
B (2)	Bu^i (f)	2	f-b	$\Delta\delta_{4,\beta}^{f}$	Non-calc.	-	-	**-**
B (2)	Am^{neo} (g)	3	g-b	$\Delta\delta_{4,\beta}^{g}$	Non-calc.	-	-	**-**
B (2)	Bu^s (h)	1	h-c	$\Delta\delta_{4,\beta}^{h}$	Non-calc.	-	-	**-**
B (2)	Am^t (k)	3	k-d	$\Delta\delta_{3,\beta}^{k}$	Non-calc.	-	-	**-**

As we can see from Table 5 **absolute values** of all “non-crossed” **differential parameters** $\Delta\delta_4^{\mathbf{C,Nj}}$ used as addends while calculating mean values of parameters $\Delta\delta_{4,\beta}^{j}$ **do not exceed 0.10 ppm (i.e. value of experimental error).** This value is five-times less than the value of conditional boundary between “insignificant” and “considerable” parameters. Therefore all five mean parameters of *para*-type $\Delta\delta_{4,\beta}^{j}$ we did not calculate and did not present them in Table 9. Their further examination is to no purpose.

III.2. Ratio between mean parameters by value and sign

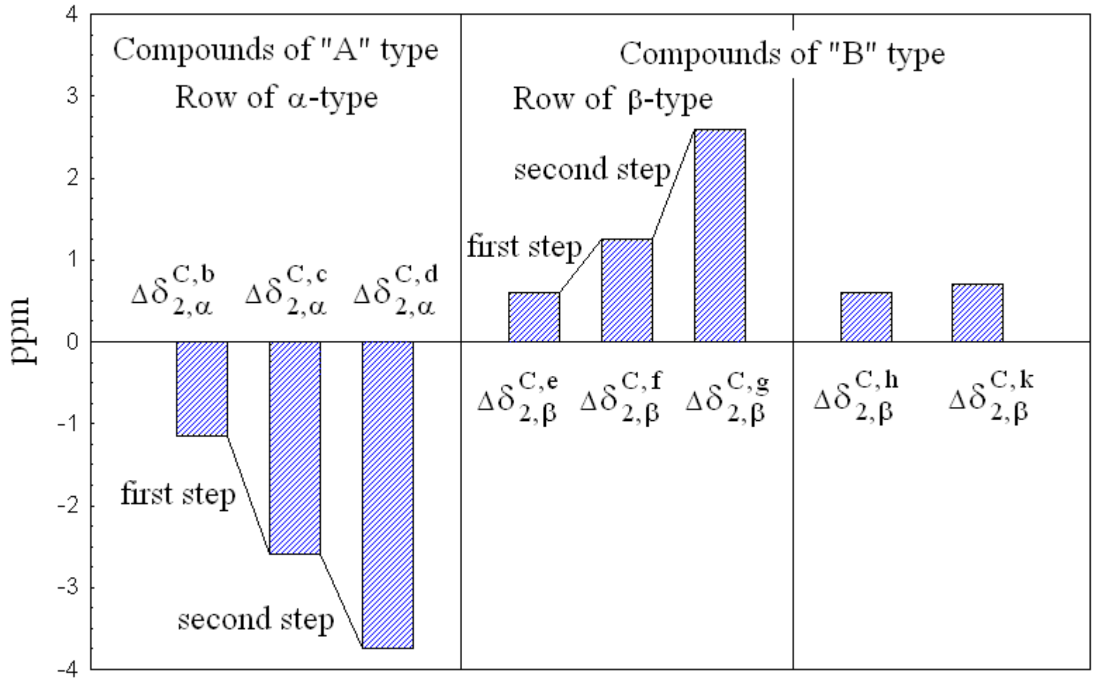
All given in Tables 6-9 mean differential parameters $\Delta\delta_i^j$ we rounded to the values divisible by 0.05 ppm and represented as diagrams in Fig. 1-3.

Fig. 1.



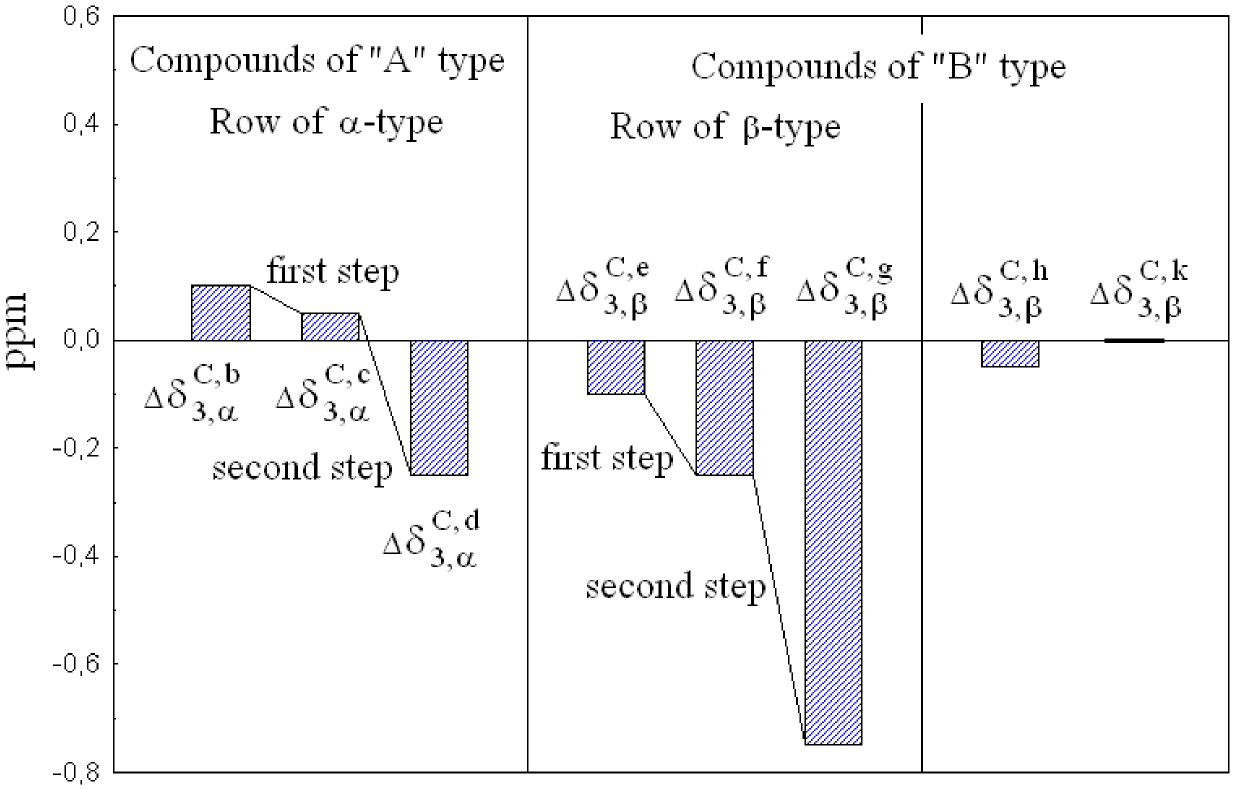
The values of mean differential parameters $\mathbf{\Delta\delta_1^{C,j}}$

Fig. 2.



The values of mean differential parameters $\mathbf{\Delta\delta_2^{C,j}}$

Fig. 3.



The values of mean differential parameters $\mathbf{\Delta\delta_3^{C,j}}$

III.2.1. Three-termed rows of mean parameters

Having enough experimental data we would be able to construct **all 4** possible **three-termed "differential rows" of mean parameters of α-type.** Every of the "differential rows" has the following view: $\mathbf{\Delta\delta_{i,\alpha}^{b(1)}} \rightarrow \mathbf{\Delta\delta_{i,\alpha}^{c(2)}} \rightarrow \mathbf{\Delta\delta_{i,\alpha}^{d(3)}}$, where i = 1-4. All 4 rows of α-type parameters are "statistically valid" because every parameter in them is calculated using a great number of examples (no less than 11).

For the parameters **of β-type** it would be possible to construct 12 "differential rows". However data given in Tables 2-5 allow to construct only **3 differential rows** (not even 4)**:** $\mathbf{\Delta\delta_{i,\beta}^{e(1)}} \rightarrow \mathbf{\Delta\delta_{i,\beta}^{f(2)}} \rightarrow \mathbf{\Delta\delta_{i,\beta}^{g(3)}}$, where i = 1-3. Moreover, all parameters of these differential rows cannot be "statistically valid". Thus, the mean parameters $\Delta\delta_{i,\beta}^{f}$ are calculated using only 3 examples (instead of necessary 5 ones). The last in the rows parameters $\Delta\delta_{i,\beta}^{H,g}$ are accepted using data of only one compound – **10g**. The insufficient "statistic validation" makes the discussion results less valuable.

Only **six** three-termed differential rows (but not possible 8 rows because of the small values of $\Delta\delta_{4,\beta}^{j}$) of **mean parameters of β-type** ($\Delta\delta_{i.,\beta}^{j}$) are limited by their first terms ($\Delta\delta_{i,\beta}^{h(1)}$ or $\Delta\delta_{i,\beta}^{k(1)}$). Therefore they cannot be considered as rows by the definition.

Thus we compare only seven rows instead of possible 16 three-termed rows of both types. Four rows of α-type parameters are “statistically valid” and three rows of β-type parameters – “statistically insufficient valid”. Moreover, we’ll discuss mean parameters of first terms ($\Delta\delta_{1,\beta}^{h(1)}$, $\Delta\delta_{2,\beta}^{h(1)}$, $\Delta\delta_{3,\beta}^{h(1)}$, $\Delta\delta_{,\beta}^{k(1)}$ и $\Delta\delta_{2,\beta}^{k1)}$ $\Delta\delta_{3,\alpha}^{k(1)}$) of six non-existent three-termed rows.

III.2.2. Differential rows of α-type

III.2.2.1. Differential rows of mean parameters of *ipso*-α-type:

$\Delta\delta_{1,\alpha}^{b(1)} = +6.40$ ppm → $\Delta\delta_{1,\alpha}^{c(2)} = +11.00$ ppm → $\Delta\delta_{1,\alpha}^{d(3)} = +13.25$ ppm

1. From the spectral data for **C-1** atom one can see that all **three mean parameters of the row have positive** value (sign “+”) and their **absolute value increases** in the row. The absolute value of all three terms in the row is determined (see above) as “considerable”. Moreover, all three parameters $\Delta\delta_{1,\alpha}^{j}$ have maximum absolute values among examined differential parameters $\Delta\delta_{i}^{j}$.

Let us note that the first transfer ($\Delta\delta_{1,\alpha}^{b(1)} \rightarrow \Delta\delta_{1,\alpha}^{c(2)}$) is more abrupt than the second one and its value (4.60 ppm) is comparable with the value of the first mean parameter ($\Delta\delta_{1,\alpha}^{b(1)} = 6.40$ ppm) taking part in this transfer. The second (and the last) step (i.e. transfer $\Delta\delta_{1,\alpha}^{c(2} \rightarrow \Delta\delta_{1,\alpha}^{d(3)}$) is more smooth, i.e. the less change of chemical shift value (2.25 ppm) is observed, what is more than twice less than the first step (4.6 ppm).

2. Absolute width of intervals of all three parameters is relatively constant within the range of 0.7–0.95 ppm. By their relative widths (7-11 %) they are “narrow”. They may be considered even as “very narrow”, i.e. ($\Delta\Delta\delta_{i,rel.}^{j} \leq 10\%$). The “narrowing” of intervals takes place due to the increase of divisor at the constant dividend in above-mentioned equation. The especial attention is paid to the low value of relative width (7%) of the last two mean parameters $\Delta\delta_{1,\alpha}^{c(2)}$ и $\Delta\delta_{1,\alpha}^{d(3)}$ in the row. The narrowness of these intervals allows to suppose that the effect of “Y” substituent nature in the compounds **1-26** is not a defining factor for the formation of chemical shift of absorption of *ipso*-carbon atoms (parameters $\delta_{1,\alpha}^{c(2)}$ and $\delta_{1,\alpha}^{d(3)}$). The same assumption is logical with respect to the parameter $\Delta\delta_{1,\alpha}^{b(1)}$ with wider interval. Obviously, the **main factor** for the formation of basic spectral parameter δ_{1}^{j} – **chemical shift of carbon atoms in *ipso*-position** in *para*-alkylsubstituted derivatives of benzene – is not nature of “Y” substituent but **degree of alkyl chain branching at α-carbon atom**. We propose to examine the

influence of substituent “Y” nature on the values of differential parameters $\Delta\delta_{i,,\alpha}^{C,Nj}$ and $\Delta\delta_{i,,\beta}^{C,Nj}$ in special paper.

III.2.2.2. Differential rows of mean parameters of *ortho*-α-type: $\Delta\delta_{2,\alpha}^{b(1)} = -1.15$ ppm → $\Delta\delta_{2,\alpha}^{c(2)} = -2.60$ ppm → $\Delta\delta_{2,\alpha}^{d(3)} = -3.75$ ppm

1. From the spectral data for **C-2 and C-6** atoms one can see that in contrast to the parameters of *ipso*-α-row ($\Delta\delta_{1,\alpha}^{j}$) **all three parameters of the *ortho*-α- row**, have **negative values** (sign “-”). Their absolute value is monotone **increasing**, the same as that for the parameters $\Delta\delta_{1,\alpha}^{j}$,. For all three terms of the row the absolute value is considered as “considerable” one. Let us note that the first transfer ($\Delta\delta_{2,\alpha}^{b(1)}$ → $\Delta\delta_{2,\alpha}^{c(2)}$) is more abrupt than the second one ($\Delta\delta_{o,\alpha}^{c(2}$→ $\Delta\delta_{o,\alpha}^{d(3)}$). The values of both transfers (1.45 and 1.15 ppm) are comparable with the absolute value of the first mean parameter ($\Delta\delta_{2,\alpha}^{b(1)} = -1.15$ ppm) in the row.

2. The absolute width of all three parameters in the investigated row consecutively increases from 0.10 to 0.40 ppm. Both values may be considered as relatively low compared with the assumed value of accuracy (0.10 ppm). By the relative width (7-10%) all three intervals may be considered as “very narrow”, the same as for mean parameters of *ipso*-α-type. The low value of relative width (7%) of the mean parameter $\Delta\delta_{2,\alpha}^{c(2)}$ should be stressed. The narrowness of three intervals allows to suppose that the effect of “Y” substituent nature in the compounds **1-26** is not a defining factor for the formation of chemical shift of absorption of *ortho*-carbon atoms (parameter $\Delta\delta_{2,\alpha}^{j(n)}$), the same as for carbon atoms in *ipso*-position. Obviously, the main factor for the formation of basic spectral parameter δ_2^{j} is not substituent “Y” nature, but a degree of alkyl chain branching at α-carbon atom (i.e. the volume of space occupied by alkyl group atoms in the definite place of the molecule).

III.2.2.3. Differential rows of mean parameters of *meta*-α-type: $\Delta\delta_{3,\alpha}^{b(1)} = +0.10$ ppm → $\Delta\delta_{3,\alpha}^{c(2)} = +0.05$ ppm → $\Delta\delta_{3,\alpha}^{d(3)} = -0.25$ ppm

1. From the spectral data for **C-3 and C-5 atoms** one can see that **first two parameters** of investigated row of *meta*-α-parameters **have the positive value** (sign “+”) and the **last parameter** in the row has **negative** value (sign “-“). It means the sign inversion in the row. Let us note the tendency: the positive value of parameter decreases in every of two steps, i.e. negative values of mean parameters in the row are **monotone increasing**.

The absolute values of all three parameters in the row are considered as “insignificant”. Even the highest one ($\Delta\delta_{3,\alpha}^{d(3)}$) is twice less than the “boundary” value (0.50 ppm) between “insignificant” and “considerable” values of the mean parameter. Values of two first terms in the row given in Table 8 are even less than assumed experimental error (0.10 ppm). The first step in the row is “little” (0.05 ppm). The second step (compared with the first one) is a “sharp jump” (0.30 ppm). Its absolute value is even higher than that of the third parameter (0.25 ppm). The total “two-step” decrease of the positive chemical shift in the row is equal to 0.35 ppm and caused mainly by the “second step”.

2. The absolute width of all 3 parameters in the row exceeds their average values. It means that all 3 intervals are “wide” and even “very wide”. The relative width of two first intervals was not calculated because of the insufficient absolute value of the mean parameters; but it is calculated for the third parameter as an exceptional case.

We suppose that the **branching of alkyl chain at α-carbon atom is not the main factor affecting the value of chemical shift of *meta*-carbon atoms** of phenyl ring, in contrast to the above-mentioned rows of *ipso*-and *ortho*-carbon atoms. Probably the reason is the considerable distance between *meta*-carbon atoms and branching point. The effect of branching decreases. The small absolute values of all three terms in the row reveal about this fact. At the same time the relative influence of the substituent “Y” nature on *meta*-carbon atoms of phenyl ring increases and becomes comparable with the investigated influence of degree of branching at α-carbon atom of alkyl chain. The confirmation is the increase of relative width of every three intervals of mean parameters $\Delta\delta_{3,\alpha}^{j}$.

III.2.2.4. Differential rows of mean parameters of para-α-type: $\Delta\delta_{4,\alpha}^{b(1)} = +0.20$ ppm → $\Delta\delta_{4,\alpha}^{c(2)} = +0.30$ ppm → $\Delta\delta_{4,\alpha}^{d(3)} = -0.10$ ppm

1. From the spectral data for **C-4 atom** one can see that **first two parameters** of investigated row of *para*-α-parameters **have the positive value** (sign “+”) and the **last parameter** in the row has **negative** value (sign “-“). It means the sign inversion in the row. It is the same as for the row of meta-α-parameters described above. The above-mentioned tendency is not preserved. The positive value of the parameter increases in the first step and decreases in the second one, i.e. **it is for the first time when monotone direction of the broken line which is connected three points of the row is distorted.**

The absolute values of all three parameters in the row are considered as “insignificant”, the same as above. Even the highest one ($\Delta\delta_{4,\alpha}^{d(3)}=0.30$ ppm) is almost twice less than the “boundary” value (0.50 ppm) between “insignificant” and “considerable” values of the mean parameter. The absolute value of the third term in the row given in Table 9 is less than assumed experimental error (0.10 ppm). The analogies described above for the row of meta-α-parameters are the same here. The first step in the row is "little" (0.10 ppm). The second step is a "sharp jump" (0.40 ppm). The total "two-step" decrease of the positive chemical shift in the row is equal to 0.30 ppm and caused only by the "second step". It is the general effect that the ratio between mean parameters is the same in both compared rows (i.e. the row $\Delta\delta_{3,\alpha}^{b(1)} \rightarrow \Delta\delta_{3,\alpha}^{c(2)} \rightarrow \Delta\delta_{3,\alpha}^{d(3)}$ and the row $\Delta\delta_{4,\alpha}^{b(1)} \rightarrow \Delta\delta_{4,\alpha}^{c(2)} \rightarrow \Delta\delta_{4,\alpha}^{d(3)}$). The exclusion is first two terms of the row, where reverse order of parameter values is observed. In the row of *para*-α-parameters the values $\Delta\delta_{4,\alpha}^{j}$ are shifted on average by+0.15 ÷ +0.20 ppm compared with corresponding values $\Delta\delta_{3,\alpha}^{j}$ in the *meta*-α-row.

2. The absolute width of all 3 parameters in the row (approximately 0.40 ppm) exceeds their average values. It means that all 3 intervals are "wide". The relative width of two first intervals was calculated as an exceptional case. The width of the third interval was not calculated because of the insufficient absolute value of $\Delta\delta_{4,\alpha}^{d}$ parameter.

We suppose that the **branching of alkyl chain at α-carbon atom is not the main factor affecting the value of chemical shift of *para*-carbon atoms** of phenyl ring, in contrast to the above-mentioned rows of *ipso*-and *ortho*-carbon atoms but the same as for *meta*-α-parameters. Probably due to the longest distance from branching point the effect of branching decreases even greater. The small absolute values of all three terms in the row reveal about this fact. At the same time the relative influence of the substituent "Y" nature on *para*-carbon atoms of phenyl ring increases and becomes comparable with the investigated influence of degree of branching at α-carbon atom of alkyl chain. The confirmation is the increase of relative width of every three intervals of mean parameters $\Delta\delta_{4,\alpha}^{j}$.

On the other hand, it should be noted that the influence of branching in alkyl substituent on the most outlying *para*-carbon atom (C-4) may be even greater than the same influence on *meta*-carbon atoms (C-3 and C-5). To our mind, it follows from the comparison of parameters which are maximal by their absolute value in both rows. Thus, the parameter $|\Delta\delta_{4,\alpha}^{c(2)}| = 0.30$ ppm in *para*-α-row is greater than the parameter $|\Delta\delta_{3,\alpha}^{d(3)}| = 0.25$ ppm in *meta*-α-row. The same situation was observed by us earlier [10] while studying the effect of carbon chain branching in alkyl part of alkylbenzoates on the basic spectral parameters – chemical shifts – of phenyl fragment carbon atoms. Possibly, both phenomena have the same or similar nature.

III.2.3. Differential rows of β-type

III.2.3.1. Differential rows of mean parameters of *ipso*-β-type: $\Delta\delta_{1,\beta}^{e(1)} = -1.55$ ppm → $\Delta\delta_{1,\beta}^{f(2)} = -2.50$ ppm → $\Delta\delta_{1,\beta}^{g(3)} = -4.55$ ppm

1. For **C-1 carbon** atom all three parameters of ***ipso*-β-row**, in contrast to the row of *ipso*-α-parameters, have **negative value** (sign "-"). But the **absolute value of the parameters monotonically increases**. All three terms in the row are considered as "considerable" ones. The total "two-step" increase of absolute value of chemical shift is 3.00 ppm, what is twice greater than the absolute value of the first term $|\Delta\delta_{1,\beta}^{e(1)}|$ = 1,55 ppm in the row. The first step is smooth (≈1 ppm) and the second one is more abrupt (≈2 ppm). It should be noted that the value of first ("little") step in the row of *ipso*-β-parameters is twice less than that of the second step (it is the same, as in the row of *meta*-α-parameters, but differ from ipso-α- and ortho-α-parameters). The values of both "steps" and two first parameters of the rows are comparable between each other (from 1.0 to 2.5 ppm), but all of them are less than the value of third parameter in the row $|\Delta\delta_{1,\beta}^{g(3)}|$ = 4.55 ppm.

It should be noted the pairwise **similarity of absolute values** of terms in *ortho*-α-row (1.15→2.60→3.75) and ***ipso*-β**-row (1.55→2.50→4.55) **excluding the negative sign** for all terms of the latter row. At the same time the absolute values of parameters of both mentioned rows are considerably less (in 3-5 times) than those of *ipso*-α-row (6.40→11.00→13.25). The possible reason of observed similarity of corresponding parameters of *ortho*-α- and *ipso*-β-row is the **comparable distance** between investigated carbon atom and **branching point** in the chain of alkyl substituent. In contrast to these rows the distance between *ipso*-carbon atom and branching point in the "nearer" *ipso*-α-row is shorter by one C-C bond.

2. It is advisable to consider the absolute width of intervals only in the case of the first parameter because this parameter is "statistically valid". We consider this interval as "very narrow" (relative width $\Delta\Delta\delta_{1,rel.}^{e}$ is 8%) because of its little absolute width ($\Delta\Delta\delta_{1,abs.}^{e}$ = 0.12 ppm) at "considerable" absolute value of mean parameter $\Delta\delta_{1,\beta}^{e(1)}$ (1.55 ppm). Its absolute width is the least among all analogous values given in Tables 6-9. This width is few times less than values calculated for all 4 α-rows (from 0.15 to 0.95 ppm, excluding width of the interval $\Delta\Delta\delta_{2,abs.}^{e}$ = 0.11 ppm) and approximately equal to the accuracy of measurements (0.10 ppm). We observed the narrowness of mean parameter $\Delta\delta_{1,\beta}^{f(2)}$, the relative width ($\Delta\Delta\delta_{1,rel.}^{f}$) of which is 8%. However, this mean parameter is "statistically insufficient valid".

III.2.3.2. Differential rows of mean parameters of *ortho*-β-type:

$\Delta\delta_{2,\beta}^{e(1)} = +0.60$ ppm → $\Delta\delta_{2,\beta}^{f(2)} = +1.25$ ppm → $\Delta\delta_{2,\beta}^{g(3)} = +2.60$ ppm

1.For **C-2 and C-6 carbon** atoms all three parameters of ***ortho*-β-row**, in contrast to the row of *ipso*-β-parameters, have **positive value** (sign "+"). The **absolute value of the parameters monotonically increases**. All three terms in the row are considered as "considerable" ones.

The total "two-step" increase of absolute value of chemical shift is 2.00 ppm, what is in three times greater than the absolute value of the first term $|\Delta\delta_{2,\beta}^{e(1)}| = 0,60$ ppm in the row. The same as for *ipso*-β-parameters, the first step is smooth (0.65 ppm) and the second one is more abrupt (1.35 ppm), i.e. the value of first ("little") step in the row of *ipso*-β-parameters is twice less than that of the second step. The values of both "steps" and two first parameters of the rows are pairwise equal to each other (approximately by 0.6 and 1.3 ppm), but they are less than the value of third parameter in the row $|\Delta\delta_{2,\beta}^{g(3)}| = 2.60$ ppm.

It is interesting that **similarity of absolute values** of "equidistant" rows of ***meta*-α-parameters** (+0.10→+0.05→-0.25) **and ortho-β-parameters** (+0.60→+1.25→2.60) **is absent** because every **absolute values** of the latter row is greater of the corresponding parameter of the first row **by order**. On the other hand, the absolute values of every term of *ortho*-β-row are twice less than those of corresponding parameters of *ipso*-β-row which is situated nearer to the branching point of alkyl chain (cf. in pairs: 1.55 and 0.60; 2.50 and 1.25; 4.55 and 2.60). However such changes (decrease) of compared parameters are less by value than above-mentioned decrease between parameters of *ipso*-β-row and *ipso*-α-row (cf. ≈2 against 3-5). The same decrease of compared parameters by value (≈ 3-5) is also noticed between parameters of *ortho*-α-row and *ipso*-α-row.

2. It is advisable to consider the absolute width of intervals only for the first term $\Delta\Delta\delta_{2,abs.}^{e}$ in the row because this parameter is "statistically valid". We consider this interval as "narrow" (relative width $\Delta\Delta\delta_{2,rel.}^{e}$ is 17%) because of its little absolute width ($\Delta\Delta\delta_{2,abs.}^{e} = 0.10$ ppm) at "considerable" absolute value of mean parameter $\Delta\delta_{2,\beta}^{e(1)}$ (0.60 ppm). Its absolute width is the least among all analogous values given in Tables 6-9 and approximately equal to the accuracy of measurements (0.10 ppm). We observed the narrowness of "statistically insufficient valid" mean parameter $\Delta\delta_{2,\beta}^{f(2)}$, the relative width ($\Delta\Delta\delta_{2,rel.}^{f}$) of which is 8%, the same as for above-mentioned interval $\Delta\Delta\delta_{1,rel.}^{f}$.

III.2.3.3. Differential rows of mean parameters of *meta*-β-type: $\Delta\delta_{3,\beta}^{e(1)}$ = -0.10 ppm → $\Delta\delta_{3,\beta}^{f(2)}$ = -0.25 ppm → $\Delta\delta_{3,\beta}^{g(3)}$ = -0.75 ppm

1. For **C-3 and C-5 carbon** atoms all three parameters of ***meta*-β-row** have **negative value** (sign "-"), the same as for *ipso*-β-parameters but in contrast to the row of *ortho*-β-parameters. The **absolute value of the parameters monotonically increases**. Two first terms in the row are considered as "insignificant" ones and only third term is "considerable" one. The first step is smooth (0.15 ppm) and the second one has "sharp jump" (0.50 ppm). The total "two-step" increase of absolute value of chemical shift is 0.65 ppm, what is in 6.5 times greater than the absolute value of the first term $\left|\Delta\delta_{3,\beta}^{e(1)}\right|$ = 0,10 ppm in the row. It is almost fully determined by the "second step".

It is interesting that **similarity of absolute values** of "equidistant" rows of ***para*-α-parameters** (+0.20→+0.30→-0.10) **and *meta*-β-parameters** (-0.10→+0.25→0.75) **is absent.** At the same it should be noted that absolute values of every term of *meta*-β-row are 3-6 times less than those of corresponding parameters of *ortho*-β-row which is situated nearer to the branching point of alkyl chain (cf. in pairs: 0.60 and 0.10; 1.25 and 0.25; 2.60 and 0.75). Such decrease of compared parameters is almost equal by value to the above-mentioned decrease between parameters of *ipso*-β-row and *ipso*-α-row (approximately in 3-5 times).

2. It is inexpediently to consider the absolute width of intervals for the first term $\Delta\Delta\delta_{3,abs.}^{j}$ in the investigated row because of too small value of mean parameter ($\Delta\delta_{3,\beta}^{e(1)}$ = -0.10 ppm) which is the same as experimental error. Other mean parameters of the second and third terms of the row are "statistically insufficient valid", therefore the discussion of their intervals width is also inexpediently.

3. In contrast to the other types of carbon atoms of phenyl ring (*ipso*-, *ortho*- and *para*-) we received **unexpected results** compared maximal by absolute values parameters in *meta*-rows (i.e. *meta*-α- and *meta*-β-rows). The value of ***meta*-α-**parameter $\left|\Delta\delta_{3,\alpha}^{d(3)}\right|$ = 0.25 ppm (maximum in *meta*-α-row) is in **three times less** than the value of ***meta*-β-**parameter $\left|\Delta\delta_{3,\beta}^{d(3)}\right|$ = 0.75ppm (maximum in *meta*-β-row)!

As it was mentioned above, the absolute values of *para*-β-parameters are close to zero, therefore the fourth possible row of *para*-parameters $\Delta\delta_{4,\beta}^{e(1)}$→ $\Delta\delta_{4,\beta}^{f(2)}$ → $\Delta\delta_{4,\beta}^{g(3)}$ will not be discussed.

III.2.4. Mean parameters of the first terms of four possible, but non-formed differential rows:

$\Delta\delta_{1,\beta}^{h(1)}$, $\Delta\delta_{2,\beta}^{h(1)}$, $\Delta\delta_{1,\beta}^{k(1)}$ и $\Delta\delta_{2,\beta}^{k(1)}$

The same as for *para*-β-parameters, the absolute values of *meta*-β-parameters $\Delta\delta_{3,\beta}^{h(1)}$, $\Delta\delta_{,3\beta}^{k(1)}$ are close to zero, therefore they are not discussed here.

From the spectral data for **C-1 atoms** represented in Table 6 one can see that both investigated ***ipso*-β-parameters $\Delta\delta_{1,\beta}^{h(1)} = -1.15$ ppm and $\Delta\delta_{1,\beta}^{k(1)} = -1.65$ ppm have negative value** (sign “-“) (the same as other three *ipso*-β-parameters united in *ipso*-β-row, see above). Their absolute values are approximately equal to the first parameter of above-mentioned row **$\Delta\delta_{1,\beta}^{e(1)} = -1.55$** ppm. We may suggest that exchanging of one hydrogen atom for methyl group in the first variable fragment R^1 (i.e. while transfer from R^1 = H to R^1 = CH_3) in the compounds of general formula $Y\text{-}C_6H_4\text{-}C^{\alpha}Z^1Z^2\text{-}C^{\beta}R^1R^2R^3$ leads to the almost equal changes of mean parameters $\Delta\delta_{1,\beta}^{j}$ (~1.5 ppm). These changes are independent from nature of two fragments (Z^1 and Z^2), attached to C^{α}-carbon atom: $Z^1 = Z^2$ = H (parameter $\Delta\delta_{2,\beta}^{e}$), Z^1 = H, Z^2 = CH_3 (parameter $\Delta\delta_{2,\beta}^{h}$), or $Z^1 = Z^2 = CH_3$ (parameter $\Delta\delta_{2,\beta}^{k}$).

The same situation is observed comparing two *ortho*-parameters (**$\Delta\delta_{2,\beta}^{h(1)}$** = +0.60 ppm and **$\Delta\delta_{2,\beta}^{k(1)}$** = +0.70 ppm, see Table 7) with other three ***ortho*-β-parameters** united into *ortho*-β-row, except of their sign. All five parameters have **positive value (sign “+”)**. Their absolute values are practically equal to the first parameter of row (Δe→Δf→Δg), i.e. **$\Delta\delta_{2,\beta}^{e(1)} = +0.60$ ppm**. The same, as in the case of ***ipso*-β-parameters $\Delta\delta_{1,\beta}^{h(1)}$ и $\Delta\delta_{1,\beta}^{k(1)}$**, we may suppose that exchanging of one or two hydrogen atoms for methyl group in fragments Z^1 and Z^2 attached to C^{α}-carbon atom leads to the equal changes of mean parameters $\Delta\delta_{2,\beta}^{j}$ (~0.65 ppm, j = h,k)**.** These changes are independent from the nature of two fragments Z^1 and Z^2: hydrogen atoms or methyl groups.

III.3. 3-Phenylpentane is an example of type “B” compounds of the general formula $Y\text{-}C_6H_4\text{-}C^{\alpha}Z^1(C^{\beta}R^1R^2R^3)_2$.

In the Ref. [6] and [7] we found only one example of the compounds of “B” type. of the general formula **$Y\text{-}C_6H_4\text{-}C^{\alpha}Z^1(C^{\beta}R^1R^2R^3)_2$.** It is 3-phenylpentane (10I). It contains two groups ($C^{\beta}R^1R^2R^3$, where R^1=Me, and $R^2 = R^3$ = H). Therefore it would be logically to compare compound **10l** with secondary butylbenzene **10h** containing the same group $C^{\beta}R^1R^2R^3$ (where R^1=Me, and $R^2 = R^3$ = H). Fragments $C^{\beta}R^1R^2R^3$ are doubled in **10I**, hence we expected that effect of 3-pentyl group would be approximately equal to the double **β-effect** $\Delta\delta_{i,\beta}^{h(1)}$ (i.e. approximately 2 x $\Delta\delta_{i,\beta}^{h(1)}$). Let us remind that above-mentioned parameter $\Delta\delta_{i,\beta}^{h(1)}$ is typical for the first step in possible, but non-formed differential row, i.e. transfer from iso-propylbenzene **10c** (containing only one fragment $C^{\beta}R^1R^2R^3$ where $R^1 = R^2 = R^3 =$ H) to secondary butylbenzene **10h** with the same fragment $C^{\beta}R^1R^2R^3$ (but R^1=Me; $R^2 = R^3 =$ H).

We introduced additional symbols taking into account the presence of two fragments ($C^{\beta}R^1R^2R^3$, where R^1=Me, and $R^2 = R^3 =$ H) in the molecule of **10I**. As far as the parameter characterizing the transfer from cumene **10c** to secondary butylbenzene **10h** is denoted as $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{h(1)}}$, we marked the parameter characterizing the first step of two-step transfer **10c→10l,** (i.e. transfer **10h →10l**) as $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)}}$. Then, the parameter characterizing both steps of transfer **10c→10l is denoted as** $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)+l(1)}}$**.**

Absorption signals in the aromatic region of the spectrum of **10I** compound are represented in [6]. The following attributions are given: $\delta_1^{C(\mathbf{10l})[6]}$ = 145.80 ppm, $\delta_2^{C(\mathbf{10l})[6]}$ = 127.84 ppm, $\delta_3^{C(\mathbf{10l})[6]}$ = 128.16 ppm, $\delta_4^{C(\mathbf{10l})[6]}$ = 125.80 ppm. Let us calculate parameters $\boldsymbol{\Delta\delta_{i,\beta}^{l(1)}}$ for the compound **10l** (relatively to secondary butylbenzene **10h**) by the formula : $\Delta\delta_{i,\beta}^{l(1)} = \delta_i^{10l} - \delta_i^{10h}$ for i = 1-4. Parameter $\boldsymbol{\Delta\delta_{1,\beta}^{l(1)[6]}}$ = 145.80 -147.65 = **-1.85ppm**; analogously $\boldsymbol{\Delta\delta_{2,\beta}^{l(1)[6]}}$ = **+0.77ppm**; $\boldsymbol{\Delta\delta_{3,\beta}^{l(1)[6]}}$ = **-0.12 ppm**; $\boldsymbol{\Delta\delta_{4,\beta}^{l(1)[6]}}$ = **-0.02ppm.** Let us compare in pairs $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{h(1)}}$ and $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)}}$ for the various values of i: **-1.85** and **-1.18** ppm **for** i = 1; **+0.77** and **+0.65** ppm for i = 2; **-0.12 and -0.06** ppm for i = 3; **-0.02 and +0.03** ppm for i = 4. In the first three pairs the mentioned parameters are comparable between each other and have the same signs. But in every pair the absolute value of parameter $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)}}$ is greater than that of parameter $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{h(1)}}$. The fourth pair of parameters ($\Delta\delta_{\mathbf{4,\beta}}^{\mathbf{l(1)}}$ and $\Delta\delta_{\mathbf{4,\beta}}^{\mathbf{h(1)}}$) we do not consider because of their small absolute values.

Let us calculate the “two-step” parameters $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)+l(1)}}$. Thus, the parameter $\boldsymbol{\Delta\delta_{1,\beta}^{l(1)+l(1)[6]}}$ is equal to: 145.80 -148.83 = **-3.03ppm**; analogously $\boldsymbol{\Delta\delta_{2,\beta}^{l(1)+l(1)[6]}}$ = **+1.42 ppm**; $\boldsymbol{\Delta\delta_{3,\beta}^{l(1)+l(1)[6]}}$ = **-0.18 ppm**; $\boldsymbol{\Delta\delta_{4,\beta}^{l(1)+l(1)[6]}}$ = **+0.01 ppm.**

If we compare the obtained values of “two-step” parameters ($\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)+l(1)}}$) with doubled values of parameters $\boldsymbol{\Delta\delta_{i,\beta}^{h(1)}}$ we’ll receive: for **C-1 atom -3.03 ppm** against 2 x (-1.18) = **-2.36 ppm;** for **C-2 atom +1.42 ppm** against 2 x (+0.65) = **+1.30 ppm;** for **C-3** attom **-0.18 ppm** against 2 x (-0.06) = **-0.12 ppm;** for **C-4 atom +0.01ppm** against 2 x (+0.03) = +0.06 ppm. We see the approximate equality by both absolute value and sign in all three pairs (excluding abovementioned pair $\Delta\delta_{\mathbf{4,\beta}}^{\mathbf{l(1)\ +l(1)}}$ and 2 x $\Delta\delta_{\mathbf{4,\beta}}^{\mathbf{h(1)}}$). But in every pair the absolute value of “two-step” parameter $\Delta\delta_{\mathbf{i,\beta}}^{\mathbf{l(1)+l(1)}}$ is something higher than the doubled value of parameter $\boldsymbol{\Delta\delta_{i,\beta}^{h(1)}}$.

On the other hand if we compare again the values of “two-step” parameters ($\Delta\delta_{i,\beta}^{l(1)+l(1)}$) with **doubled values of parameters $\Delta\delta_{i,\beta}^{l(1)}$** we’ll receive: for **C-1 atom -3.03 ppm** against 2 x (-1.85) = **-3.70 ppm;** for **C-2 atom +1.42 ppm** against 2 x (+0.77) = **+1.54 ppm;** for **C-3** attom **-0.18 ppm** against 2 x (-0.12) = **-0.24 ppm**. We see again the approximate equality by both absolute value and sign in all three pairs. But in every pair the absolute value of “two-step” parameter $\Delta\delta_{i,\beta}^{l(1)+l(1)}$ is something lower than the doubled value of parameter $\Delta\delta_{i,\beta}^{l(1)}$.

So we can make such conclusion: the absolute value of every “two-step” parameters $\Delta\delta_{i,\beta}^{l(1)+l(1)}$ is approximately equal to doubled value every of two abovementioned “one-step” parameters. But it is something higher than the doubled value of parameter $\Delta\delta_{i,\beta}^{h(1)}$ and something lower than the doubled value of parameter $\Delta\delta_{i,\beta}^{l(1)}$.

IV. Conclusions

1. Considering NMR ^{13}C spectra of great amount of rows of disubstituted para-alkylaromatic compounds of the general formula **4-Y-C_6H_4-Alk** we confirm and “statistically validate” the conclusions made earlier in [2, 3].

2. The chain **branching** at **α-carbon** atom in alkyl substituent Alk leads to the **positive *ipso*-α-effect** and **negative *ortho*-α-effect**. At the same time if the **branching** takes place at **β-carbon** atom, it leads to the **negative *ipso*-β-** and **meta-β-effects** and **positive *ortho*-β-effect**. For both ***ipso*-carbon** atom (C-1) **and *ortho*-carbon** atoms (C-2 and C-6) **the signs of α- and β-effects** are **opposite.** For **both α- and β-effects** we observed the alternation of signs as they move away from branching point: for **α-effect** it involves **first two atoms** of phenyl ring **(C-1** and **C-2** (C-6)**); for β-effect – first three atoms** of phenyl ring **(C-1, C-2** (C-6) and **C-3** (C-5)**).**

3. **The absolute values of mean differential parameters ($\Delta\delta_i^j$)** calculated for *ipso-* (**C-1),** *ortho-* (**C-2** and C-6**)** and *meta-* (**C-3** and C-5**) carbon** atoms of **phenyl ring** and influenced by α- and β-effects **naturally decrease** as they **move away** from **branching point** of alkyl chain in the substituent Alk.

Thus, for **α-effect** the absolute values of **differential mean parameters $\Delta\delta_{i,\alpha}^{b}$** (i.e. transfer from methyl to ethyl group) are equal to: $|\mathbf{6.40}|$ (i =1) → $|\mathbf{1.15}|$ (i =2) → $|\mathbf{0.10}|$ (i =3) ; values of **differential mean parameters $\Delta\delta_{i,\alpha}^{c}$** (transfer from Alk = Me to Alk = Pr^i) are equal to: $|\mathbf{11.00}|$ (i =1) → $|\mathbf{2.60}|$ (i =2) → $|\mathbf{0.05}|$ (i =3) and values of **differential mean parameters $\Delta\delta_{i,\alpha}^{d}$** (transfer from Alk = Me to Alk = Bu^t) are equal to: $|\mathbf{13.25}|$ (i =1) → $|\mathbf{3.75}|$ (i =2) → $|\mathbf{0.25}|$ (i =3).

For **β-effect** the absolute values of the same **differential mean parameters** are: **│1.55│** (i =1) → **│0.60│**(i =2) → **│0.10│**(i =3) for parameters $\boldsymbol{\Delta\delta_{i,\beta}^{e}}$; **│2.50│** (i =1) → **│1.55│**(i =2) → **│0.25│**(i =3) for parameters $\boldsymbol{\Delta\delta_{i,\beta}^{f}}$ and **│4.55│** (i =1) → **│2.60│**(i =2) → **│0.75│**(i =3) for parameters $\boldsymbol{\Delta\delta_{i,\beta}^{g}}$**.**

4. The **absolute values** of all 6 mean **differential mean parameters** $\boldsymbol{\Delta\delta_{i}^{j}}$) (where i = 3 or 4) calculated for *para*- (**C-4**) and *meta*- (**C-3** and C-5) carbon atoms of phenyl ring and influenced by **α-effect** have the **"insignificant" absolute value** (to 0.30 ppm). Three mean **differential parameters (**$\boldsymbol{\Delta\delta_{i}^{j}}$) (i = 4) calculated for *para*-carbon atoms (**C-4**) and influenced by **β-effect** have even less values (to 0.10 ppm).

5. We suppose that the value of **β-effect** of carbon atom of phenyl ring (e.g. **C-1**) is **equal and opposite by sign to α-effect** of carbon atom which is **next in the ring** (e.g. **C-2**). The similar relation is observed between values of **β-effect of C-2 atom** and **α-effect of C-3 atom**. It means that **quantitative characteristics** of these **effects** may be **determined** by the **number of carbon-carbonic bonds** between the investigated **carbon atom** of phenyl ring and **branching point of alkyl chain**. At the same time *ipso*-α-effect is maximal for C-1 atom because the number of abovementioned bonds C-C in it is minimum and equal to one.

6. ***Para*-β-effect** is found to be negligible by value (to 0.10 ppm or it is absent at all) because investigated C-4 atom is too far from the branching point at β-carbon atom of alkyl substitutent.

7. In a case of ***meta*-carbon atoms C-3** and C-5 **β-effect** is **greater** than **α-effect** by absolute value, i.e. (│$\boldsymbol{\Delta\delta_{3,\beta}^{j}}$│)> (│$\boldsymbol{\Delta\delta_{3,\alpha}^{j}}$│).

8. **The absolute values of mean differential parameters** $\Delta\delta_{i,\beta}^{j(1)}$, where j = e,h,k for first transfer is approximately equal between each other for all three types of atoms in phenyl ring (i = 1-3), including the parameter of "one-step" $\Delta\delta_{i,\beta}^{l(1)}$ but they are twice less than parameters $\Delta\delta_{i,\beta}^{j(2)}$, characterizing the "two-step" transfer, as well as "two-step" parameters $\Delta\delta_{i,\beta}^{l(1)+l(1)}$, calculated for **10I**.

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[i] We represent basis spectral data of isobutylbenzene 10f as an example [6]: δ_2^C = 129.10 ppm and δ_3^C = 129.13 ppm or vice versa.

[**] The other meanings of symbol "Z" ($Z = -C^{\beta}R^{1}R^{2}R^{3}$) are possible. One of them (compound **10I**) is represented in the end of present paper.

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