Monoalkylbenzenes substituted by functional groups in the side chain. The effect of alkyl groups spatial structure on the chemical shift of aromatic ortho-protons in NMR[1]H spectra.

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Abstract. The analysis of aromatic proton's chemical shifts in ^{1}H NMR spectra of monoalkylbenzens with functional groups in alkyl chain was made. It is shown that (as in the case of unsubstituted analogues) increase the number of methyl groups at α-carbon atom leads to a downfield shift absorption of ortho-protons (α-effect), and with the introduction of methyl groups to the β-carbon atom is observed β-effect − upfield shift of the ortho-proton's signals.

I. Introduction.

In our previous work [1] we found interesting dependencies of ortho-protons chemical shift (δ_o^H) in monoalkylbenzenes NMR[1]H spectra upon the place and degree of branching of alkyl chain. If the branching takes place at the α-carbon atom, the shift of basic spectral parameter δ_o^H toward downfield (α-effect) is observed; the branching of alkyl chain at β-carbon atom leads to the shift toward upfield (β-effect). α-Effect has a positive value because δ_o^H value increases with the increase of amount of methyl groups in α-position. And on the contrary, β-effect has a negative value because chemical shift δ_o^H decreases with the increase of amount of branching at β-carbon atom. However, the found regularities are not general since they are not observed even at the substitution of carbon atom for silicium one in α-position of alkyl chain of alkylbenzenes **1** [1].

The natural question emerges: which classes of aromatic compounds (in addition to monoalkylbenzenes) the founded regularities apply to? We may obtain the answer while studying NMR[1]H spectra of selected aromatic compounds.

With this aim in this work we compare NMR[1]H spectra of some alkylbenzenes with functional groups in alkyl substituent and denote them as Ph-Alk. By "Alk" symbol we denote saturated alkyl groups mono-, di- and three-substituted by functional groups (X, Y, Z) at α- and β-positions. They have the common term "compounds with saturated alkyl groups". They are: phenylmethanols (**2, 3**), β-chlorethylbenzenes (**4**), α-bromatoluenes (**5**), 2-phenylacetic acids (**6**) and α,α-dimethoxytoluenes (**7**) as bifunctionally substituted.

Extended interpretation of the term "functional groups" allows to examine alkyl groups with multiple bonds C=C, C≡C and C=O as a functionalized fragment (Alk). In some cases other functional substituents are present in alkyl groups in addition to the multiple bonds. All these structures are united by the common term "compounds with unsaturated alkyl groups". Among them we studied spectral parameters of some alkenyl- (**8-11**) and alkynylbenzenes (**12**), as well as carbonyl-containing compounds (**13, 14**).

Classified data for non-functional monoalkylbenzenes (**1, 15-17**) which were described earlier [1] are also given here for the comparison.

Formation methods of compared compounds series.

Depending upon the place of alkyl chain branching in the Alk substituent all investigated compounds Ph-Alk are divided into two types: A and B. In the compounds of A type (**1, 2, 4-9, 13**) the branching takes place at α-carbon atom and in the compounds of B type (**3, 9-12, 14-17**) – at β-carbon atom. We selected such series of

compounds **1-17** which Alk substituents have maximally short alkyl chains consisting of 1 or 2 carbon atoms in the compounds of A type, and 2 or 3 carbon atoms in the compounds of type B.

We used the method of spectral parameters comparison based on assumption about virtual division of investigated compound molecule into two fragments: "invariable" and "variable" ones [1]. Thus we investigate the changes of spectral parameters in the "invariable fragment" under the influence of structural changes in "variable fragment".

In every series of compounds of type A the phenyl group C_6H_5- and α-carbon atom of Alk substituent are included in the "invariable fragment" C_6H_5–C. The variable fragments (denoted by italic) in amount from one to three (R^1, R^2, R^3) or functional groups X, Y may be added to three free valencies of alkyl substituent in "saturated" monoalkylbenzenes **1-7**. We introduced the following limitation: the variable fragments R^1, R^2, R^3 may be only hydrogen atom or methyl group. The amount of methyl groups among variable fragments R^1, R^2, R^3 we denoted as n. The maximum amount is 3 ($n_m = 3$).

Such extreme case for non-functional monoalkylbenzenes **1** is *tert*-butyl group in *tert*-butylbenzene **1d**, where all three variable fragments are methyl substituents. The opposite extreme case for compounds **1** is the methyl group in toluene **1a**, when none methyl group is among variable fragments (n = 0 and $R^1 = R^2 = R^3 = $ H). Ethyl (n = 1 in ethylbenzene **1b**) and isopropyl (n = 2 in cumene **1c**) groups are between these extreme cases. Hence, the maximum amount of series (row) terms (N) is calculated by the formula: $N = n_m + 1$. Such four-termed series is determined by us as a "normal" one and was investigated earlier [1] for the non-functionalized monoalkylbenzenes **1**. It contains all above-mentioned 4 alkyl groups and therefore may be considered as complete row. The incomplete series are those rows containing only two or three of four possible series terms.

In saturated mono-functionalized compounds of A type (**2, 4-6**) the functional substituent X arranged at α-carbon atom of the alkyl chain bounds one of three valencies; the other two ones may be bounded with two variable substituents (R^1, R^2). Correspondingly, for saturated bi-functionally substituted compounds **7** we have the possibility to vary only one variable substituent R^1. All above-mentioned is valid for compounds with unsaturated alkyl groups **8, 9, 13**.

If at α-carbon atom it is only one functional substituent X then compounds belong to the subseries AX; if there are two substituents (X and Y) – subseries AXY. The subseries AX has two variable substituents (R^1 and R^2) and maximally possible amount of methyl groups is two ($n_m = 2$). The compounds **2** and **6** are in this subseries. The subseries AXY (**4, 5, 7-9, 13**) has only one variable substituent R^1 and $n_m = 1$. The non-

functionalized monoalkylbenzenes **1** denoted as subseries A have three variable substituents (R^1, R^2, R^3), therefore $n_m = 3$.

Thus, the normal complete row in the compounds of subseries A has 4 terms ($n_m = 3$); in the compounds of subseries AX – 3 terms ($n_m = 2$) and in the compounds of subseries AXY – 2 terms ($n_m = 1$).

For the compounds of series B (compounds **3, 9-12, 14-17**) the substituents at α-carbon atom are denoted by symbols Z^1 and Z^2. Moreover, hydrogen atoms (compounds **9-11, 15-16**), methyl groups (compounds **16-17**), multiple bonds C=C, C≡C (compounds **9-12**) as well as C=O (compound **14**) may also considered as substituents. All above-mentioned for the compounds of A series with the substituent at α-carbon atom is the same for the compounds with the substituent at β-carbon atom. The normal complete row consisting of 4 compounds is given for phenones (**14**); it is denoted as subseries B. Correspondingly, the compounds of subseries BX may contain maximum 3 terms (normal series) and subseries BXY – 2 terms.

Some compounds (for example, the compound **9**) may simultaneously belong to the series A and B. Therefore while denotation of such compound in the series of compounds with greater number, the latter is given in parentheses.

Selection criteria of functionalized monoalkylbenzenes series.

To the compounds of series A and B we tried to include the compound series with the most prevailing substituents in the alkyl chain containing heteroatoms N, O, Hal. However, because of the insufficient quantity of spectral data in used informational sources [2, 3] (see below) and insufficient resolutions of available NMR[1]H spectra for the compounds of the series A [3], we have not reliable information concerning nitrogen-containing substituents to construct even incomplete row. It is possible to construct only two incomplete rows of compounds with haloid-containing substituents (series of compounds **4** and **5**).

For the compounds of the series B we found [cf. 2, 3] spectral data for only two complete rows: phenones (**14**) and described earlier [1] alkylbenzenes (**15**). The both rows are structurally allied with the compounds of the series A (**13** and **1**, respectively). Therefore in order to attract additional reliable spectral data we decided to include some incomplete series of non-functionalized monoalkylbenzenes which are structurally connected with the compounds **1** of the type A (compounds **16-17**).

Changes necessary for the conversion of incomplete rows to complete rows with less number n_m ("adapted" rows)

Above-mentioned incomplete rows of the compounds **3-5, 16, 17** we converted

into more <u>adapted rows</u> using <u>hydrogen atoms as substituents X and Y</u> (in formulae and tables these groups are marked by bold type). Such action converts them into the complete normal rows of the compounds of subseries AXY or BXY.

Thus the following complete rows of the compounds **1-17** were constructed:

Series A

$C_6H_5-C^{\alpha}(R^1)(R^2)(R^3)$ or $C_6H_5-C^{\alpha}(R^1)(R^2)X$ or $C_6H_5-C^{\alpha}(R^1)XY$. In all cases R^1, R^2 and R^3 are H or CH_3.

<u>Subseries A.</u> $C_6H_5-C^{\alpha}(R^1)(R^2)(R^3)$ (**1**): Substituents $X = R^3$, $Y = R^2$

<u>Subseries AX:</u> $C_6H_5-C^{\alpha}(R^1)(R^2)X$. Substituents: $X = OH$ (**2**); $COOH$ (**6**), $Y = R^2$.

<u>Subseries AXY:</u> $C_6H_5-C^{\alpha}(R^1)XY$. Substituents: $X = CH_2Cl$, $Y = $ **H** (**4**); $X = Br$, $Y = $ **H** (**5**); $X = Y = OCH_3$ (**7**), $X + Y = (=CH_2)$ (**8**); $X + Y = (=CH-Ph)$ (**9**); $X + Y = (=O)$ (**13**).

Series B

$C_6H_5-C^{\alpha}(Z^1)(Z^2)-C^{\beta}(R^1)(R^2)(R^3)$. In all cases R^1, R^2 and R^3 are H or CH_3.

<u>Subseries B</u>: $C_6H_5-C^{\alpha}(Z^1)(Z^2)-C^{\beta}(R^1)(R^2)(R^3)$, $X = R^3$, $Y = R^2$. Substituents: $(Z^1 + Z^2) = (=O)$ (**14**); $Z^1 = Z^2 = H$ (**15**).

<u>Subseries BX:</u> $C_6H_5-C^{\alpha}(Z^1)(Z^2)-C^{\beta}(R^1)(R^2)X$. Substituents: $Z^1 = H$, $(Z^2 + X)$ — double bond $C^{\alpha} = C^{\beta}$, $Y = R^2$ (**10**).

<u>Subseries BXY:</u> $C_6H_5-C^{\alpha}(Z^1)(Z^2)-C^{\beta}(R^1)XY$. Substituents: $Z^1 = CH_3$, $Z^2 = OH$, $X = Y = $ **H** (**3**); $Z^1 = H$, $(Z^2 + X)$ — double bond $C^{\alpha} = C^{\beta}$; $Y = Ph$ (**9**); $Z^1 = H$, $(Z^2 + X)$ — double bond $C^{\alpha} = C^{\beta}$; $Y = (-CH=O)$ (**11**); Z^1, $Z^2 + X$, Y — triple bond $C^{\alpha} \equiv C^{\beta}$ (**12**); $Z^1 = H$, $Z^2 = CH_3$, $X = Y = $ **H** (**16**); $Z^1 = Z^2 = CH_3$, $X = Y = $ **H** (**17**).

Spectral parameters used for the comparison

In the basic NMR ^1H spectral parameters $\delta_o^{H,N(i)}$ of the compounds of type A and B – the chemical shift of ortho-protons - the number of the compound is denoted by numeral N and the type of alkyl substituent is denoted by letter (i). It depends upon the amount (n) of methyl groups among variable fragments R^1, R^2 and R^3. Comparing NMR ^1H spectra of the compounds **1-17** with various functional substituents in the alkyl chain the use of differential spectral parameters ($\Delta\delta_o^H$) instead of basic ones (δ_o^H) is more advisable because of the great scattering of $\delta_o^{H,N(n)}$ values. The differential spectral parameters are calculated by formula:

$$\Delta\delta_o^{H,N(n)} = \delta_o^{H,N(n)} - \delta_o^{H,N(0)},$$

where differential spectral parameter $\Delta\delta_o^{H,N(n)}$ is a difference between the value of ortho-protons chemical shift $\delta_o^{H,N(n)}$ of the compound N_n and the same value $\delta_o^{H,N(0)}$ of substance which is chosen as a standard for the first term in the row, i.e. N_0 compound, when all substituents $R^1 = R^2 = R^3 = H$.

II. Experimental data

The choice of investigated classes of compounds is explained exclusively by the availability of reliable basic spectral parameters ($\delta_o^{H,N(n)}$) given in the literature [2, 3] sufficient to form corresponding series. These data are obtained in $CDCl_3$. The selection of mentioned references is based on the considerations of their "compatibility" [1, 4, 5] which were represented earlier.

NMR ^1H spectra without author's attribution of signals given in [2] were recorded using high-frequency instruments (300 MHz). The accuracy was 0.01 ppm. Among spectra given in [3] we selected only those obtained using instruments with the frequency of 400 MHz. Authors show values of $\delta_o^{H,N(n)}$ determined with the accuracy of 0.001 ppm. The values of $\delta_o^{H,N(n)}$ basic parameters given in [2] and [3] are in agreement with each other. In all cases we preferred data from [2] because we have the possibility to control attribution of signals $\delta_o^{H,N(i)}$ additionally by enlargement of that spectra part we are interested in. Thus we diminish the risk of insertion of mistakes which may be done by authors [3]. The data from [3] were used only in the absence of the same information in [2] and to compare the data from both references.

We attributed a doublet with intensity of 2H and constants $^3J = 7$–9 Hz to the adsorption of ortho-protons in NMR ^1H spectra given in [2]. The numerical values of δ_0^H parameters were equal to the value of center between peaks of the doublet with the accuracy of 0.005 ppm. The difference between the values of the same parameter δ_0^H given in [2] and [3] usually was less than 0.02 ppm; the same value was accepted as an average experimental error.

The values of literary basic parameters $\delta_0^{H,N(i)}$, as well as calculated differential spectral parameters $\Delta\delta_0^{H,N(i)}$ for the compounds of <u>series A</u>: **1, 2, 4-9, 13** are represented in Table 1 and for the compounds **3, 9-12, 14-17** – in Table 2. In some cases (e.g. for the compounds **2a** and others), when NMR ^1H spectrum has insufficient resolution, the whole range of δ_i^H values is given in the Table as the value of basic spectral parameter $\delta_0^{H,N(i)}$. The differential spectral parameters $\Delta\delta_0^{H,N(i)}$ were calculated in such a case as a difference between $\delta_0^{H,N(i)}$ parameter and δ^H value of low field boundary of mentioned range and given with a symbol "$\geq$" (e.g. $\Delta\delta_0^{H,2c} \geq 0.12$ ppm).

Table 1

Values of basic $\delta_o^{H,N(i)}$ and differential $\Delta\delta_o^{H,N(i)}$ spectral parameters of the compounds **1–9**, **13** of A type

Compound number	Compound	X(R3)	Y(R2)	*R1*	Ref.	$\delta_o^{H,N(i)}$	$\Delta\delta_o^{H,N(i)}$
1a	Toluene	H	H	H	[2]	7.14	0.00
1b	Ethylbenzene	CH₃	H	H	[2]	7.18	+0.04
1c	Cumene	CH₃	CH₃	H	[2]	7.21	+0.07
1d	Tert-butylbenzene	CH₃	CH₃	CH₃	[2]	7.385	+0.245
2a	Benzyl alcohol	OH	H	H	[2]	7.19−7.34	[0.00]
2b	α-Methylbenzyl alcohol	OH	CH₃	H	[2]	7.19−7.35	—
2c	α-Dimethylbenzyl alcohol	OH	CH₃	CH₃	[2]	7.46	≥ +0.12
4a	β-Chlorphenylethane	CH₂Cl	**H**	H	[2]	7.19−7.33	[0.00]
4b	α-Methyl-β-chlorphenylethane	CH₂Cl	**H**	CH₃	[2]	7.36	≥ +0.03
5a	Benzylbromide	Br	**H**	H	[2]	7.23−7.39	[0.00]
5b	α-Bromphenylethane	Br	**H**	CH₃	[2]	7.415	≥ +0.025
6a	Phenylacetic acid	COOH	*H*	H	[2]	7.22−7.35	[0.00]
6b	2-Phenylpropionic acid	COOH	*CH₃*	H	[2]	7.21−7.35	—
6c	Dimethyl phenylacetic acid	COOH	*CH₃*	CH₃	[3]	7.394	≥ +0.044
7a	α, α-Dimethoxytoluene	OCH₃	OCH₃	H	[2]	7.445	0.00
7b	α, α-Dimethoxyethylbenzene	OCH₃	OCH₃	CH₃	[2]	7.495	+0.05
8a	Styrene	=CH₂		H	[2]	7.39	0.00
8b	α-Methylstyrene	=CH₂		CH₃	[2]	7.45	0.06
9a	Stilbene	=CHPh		H	[2]	7.485	0.00
9a	α-Methylstilbene	=CHPh		CH₃	[2]	7.505	+0.02
13a	Benzaldehyde	=O		H	[2]	7.87	0.00
13b	Acetophenone	=O		CH₃	[2]	7.945	+0.075

Concerning the compounds Alk-C_6H_5 of the <u>series B</u> we succeeded (by above-mentioned reasons) to compose only two normal complete rows for the compounds **14** and **15** of subseries B, one complete trinomial row for the compound **10** of subseries BX and three complete binomial rows for the compounds **9, 11, 12** of subseries BXY. For the other compounds (**3, 16, 17**) we used the method of incomplete normal rows conversion into complete adapted ones of subseries BXY. Table 2 represents the values of basic $\delta_o^{H,N(i)}$ and calculated differential $\Delta\delta_o^{H,N(i)}$ spectral parameters for these compounds.

Table 2

Values of basic $\delta_o^{H,N(i)}$ and differential of the compounds **3**, **9–12**, **14–17** of B type

Compound number	Compound	Z^1	Z^2	R^3 (X)	R^2 (Y)	R^1	Ref.	$\delta_o^{H,Ni}$	$\Delta\delta_o^{H,Ni}$
3a	α-Dimethylbenzyl alcohol	OH	CH_3	**H**	**H**	H	[2]	7.46	0.00
3b	α-Ethyl-α-methylbenzyl alcohol	OH	CH_3	**H**	**H**	CH_3	[2]	7.42	−0.04
9a	Stilbene	**H**	Double bond C=C		Ph	H	[2]	7.485	0.00
9b	α-Methylstilbene	**H**	Double bond C=C		Ph	CH_3	[2]	7.30-7.38	≤ −0.105
8a (**10**a)	1-Phenylethene (styrene)	**H**	Double bond C=C		H	H	[2]	7.39	0.00
10b	E-1-Phenylpropene-1	**H**	Double bond C=C		H	CH_3	[2]	7.31	−0.08
10c	1-Phenyl-2-methylpropene-1	**H**	Double bond C=C		CH_3	CH_3	[2]	7.21	−0.18
11a	*Trans*-cinnamic aldehyde	**H**	Double bond C=C		CH=O	H	[2]	7.555	0.00
11b	α-Methyl-*trans*-cinnamic aldehyde	**H**	Double bond C=C		CH=O	CH_3	[2]	7.52	–0.035
12a	Phenylacetylene	Triple bond C≡C				H	[2]	7.485	0,00
12b	Phenylmethylacetylene	Triple bond C≡C				CH_3	[2]	7.385	−0,10
13b (**14**a)	1-Phenylethanone (acetophenone)	=O	H		H	H	[2]	7.945	0.00
14b	1-Phenylpropanone (propiophenone)	=O	CH_3		H	H	[2]	7.955	+0.01
14c	1-Phenyl-2-	=O	CH_3		CH_3	H	[2]	7.955	+0.01

	methylpropanone (isobutyrophenone)								
14d	1-Phenyl-2,2-dimethyl-propanone (phenyl-*tert*-butylketone)	=O		CH$_3$	CH$_3$	CH$_3$	[2]	7.685	-0.26
1b (**15**a)	Ethylbenzene	**H**	**H**	H	H	H	[2]	7.18	0.00
15b	Propylbenzene	**H**	**H**	CH$_3$	H	H	[2]	7.16	−0.02
15c	Isobutylbenzene	**H**	**H**	CH$_3$	CH$_3$	H	[3]	7.14	−0.04
15d	Neopentylbenzene	**H**	**H**	CH$_3$	CH$_3$	CH$_3$	[2]	7.11	−0.07
1c (**16**a)	Isopropylbenzene (cumene)	**H**	**CH$_3$**	**H**	**H**	H	[2]	7.21	0.00
16b	*Sec*-butylbenzene	**H**	**CH$_3$**	**H**	**H**	CH$_3$	[2]	7.17	−0.04
1d (**17**a)	1-Phenyl-1,1-dimethylethane (*tert*-butylbenzene)	**CH$_3$**	**CH$_3$**	**H**	**H**	H	[2]	7.385	0.00
17b	1-Phenyl-1,1-dimethyl-propane (*tert*-pentylbenzene)	**CH$_3$**	**CH$_3$**	**H**	**H**	CH$_3$	[3]	7.31	−0.075

III. Results and Discussion

Compounds of the series A

In all rows of the compounds of the <u>A</u> type (**1, 2, 4-9, 13**) the α-effect is present which was described earlier [1]. Its value probably depends upon the structural peculiarities of the substituents X and Y.

One can see from Table 1 the definite, sometimes saltatory, low-field shift of δ_0^H value in five rows of the compounds of the series A which contain functional substituents X and/or Y (**2, 6-8, 13**) as well as in unsubstituted row of compounds **1**. This shift takes place while transition from next to last term of the row (n-1), where one hydrogen atom still remains as a substituent (R^I = H), to the last term of the row (n) – permethylsubstituted compound, where all substituents are methyl groups. The shift is less for stilbenes **9**. The given data confirm the previous explanation based on the conformational analysis [1] of the reasons of salutatory increase of δ_0^H value while transition just to the last (permethylsubstituted) term of the row in non-functionalized monoalkylbenzenes (**1**).

In NMR^{1}H spectra of the first terms of row of benzyl alcohol derivatives (**2a, 2b**) and 2-phenyl-alkane acids (**6a, 6b**), as well as haloid-containing compounds (**4a, 5a**) all

five ortho-, meta- and para-protons of phenyl ring absorb in very narrow area – less than 0.15 ppm. Therefore investigations of NMR[1]H spectra obtained even at high-frequency instruments (300 MHz) sometimes do not allow to separate the signal of two ortho-protons from the signals of other types of aromatic protons.

The opposite situation is observed for the last terms of these rows – compounds **2c, 4b, 5b** and **6c**. Along with the mentioned low-field shift of ortho-protons signal we observe the sufficiently high resolution of the signals for all three types of protons. Table 1 represents the minimum value of $\Delta\delta_0^{H,N(n)}$ parameter (usually no less than 0.03 ppm), whereas in fact this parameter may be greater (within the range from 0.05 to 0.2 ppm).

In binomial rows of the compounds **7, 8, 9, 13** we also observe the low-field shift of the signal of the last (second) term $N_{(1)}$ compared with the adsorption of the first term $N_{(0)}$.

The diagrams represented in Fig. 1 illustrate the typical changes of $\Delta\delta_0^{H,N(n)}$ differential parameters for the series of compounds **1, 7, 13** of the type A.

Fig. 1.
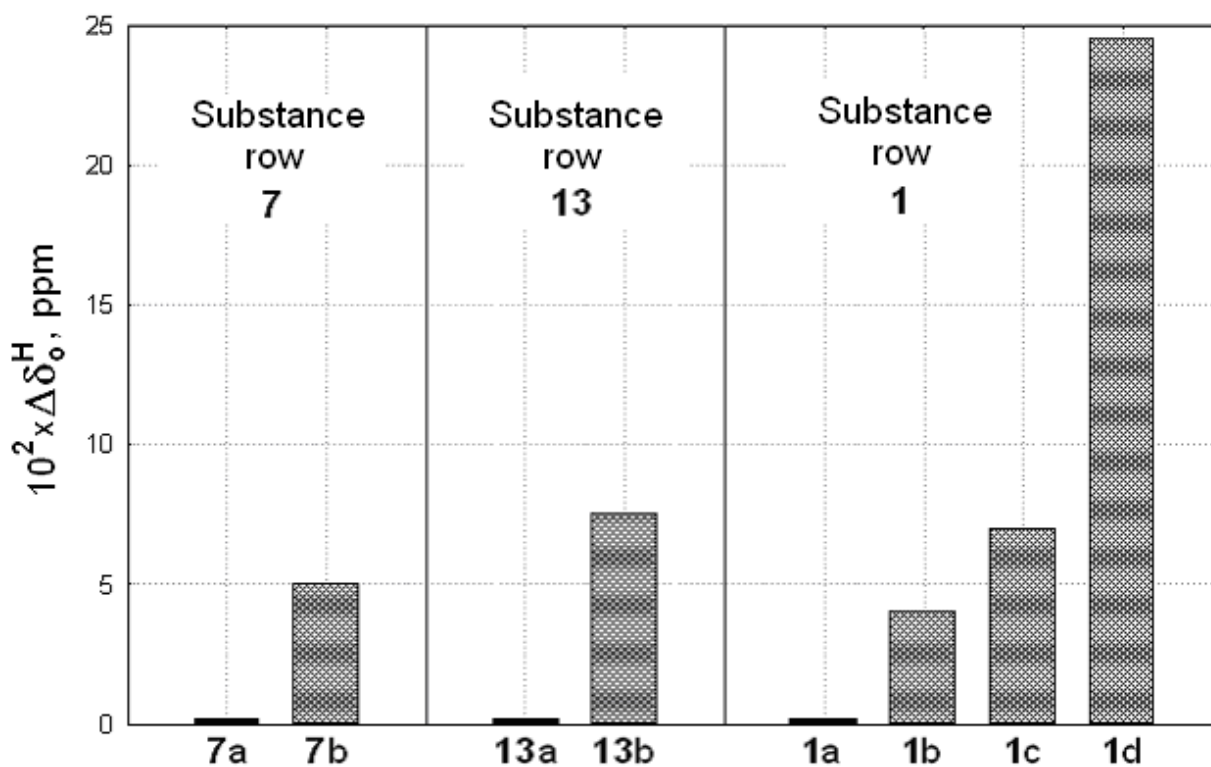
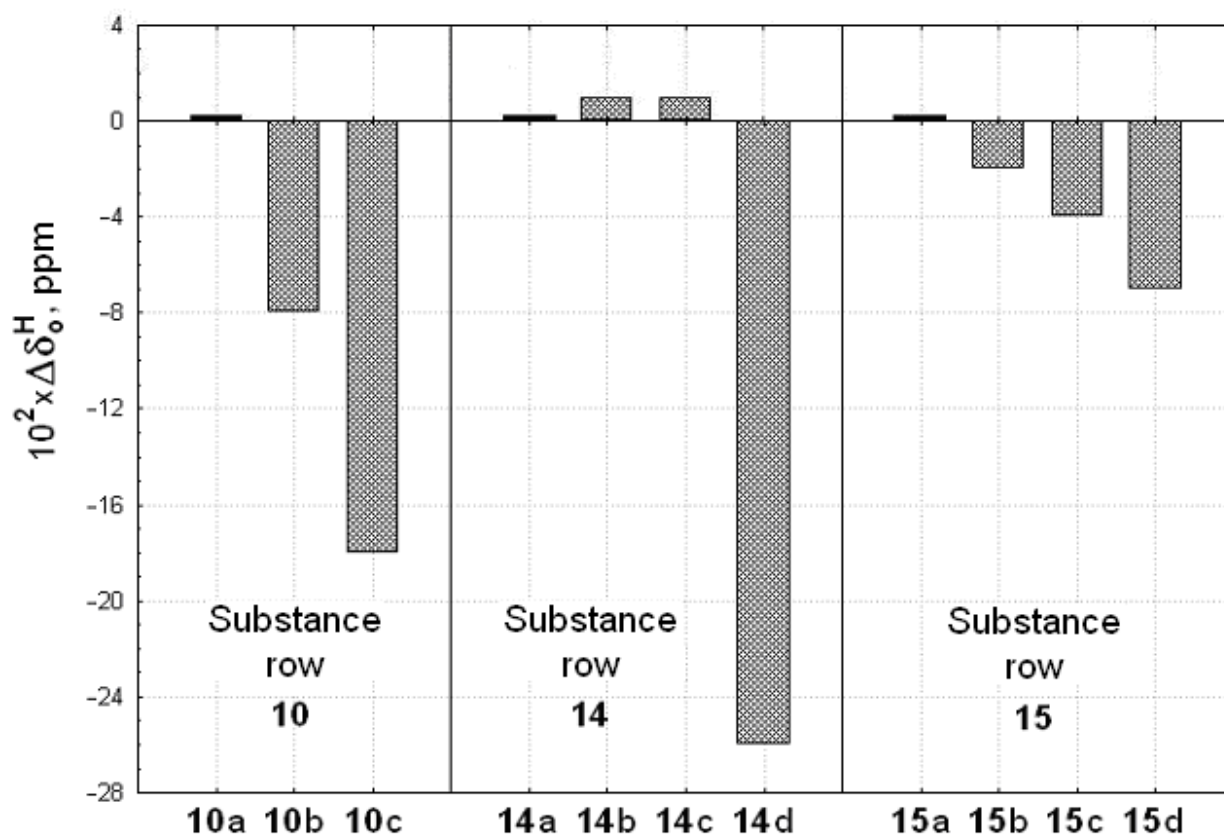The changes of $\Delta\delta_0^{H,N(n)}$ differential parameters in the series of compounds **1, 7, 13**

Compounds of the type B.

All conclusions similar to the mentioned for the A type may be done in a case when

hydrogen atoms are substituted for methyl groups at β-carbon atom for the rows of compounds of the B type (**3, 9-12, 14-17**). These conclusions confirm the explanation [1] of observed β-effect. But for the compounds of the B type we found still less reliable rows than for the compounds of the A type. Only in two cases (compounds **14** and **15**) we have data to compose normal complete four-termed row. The normal complete trinomial row of the compounds **10** also confirms the presence of β-effect. The data for three binomial rows (**9, 11, 12**) and three transformed into adapted complete binomial rows (**3, 16, 17**) do not contradict the presence of β-effect. Thus in the case of compounds of the B type the available data confirm the presence of β-effect in monoalkylbenzenes containing functional substituents in alkyl groups.

Fig. 2 represents the changes of $\Delta\delta_0^{H,N(n)}$ differential parameters for the most informative rows of the compounds **10, 14, 15** of the B type.

Fig. 2

Changes of $\Delta\delta_0^{H,N(n)}$ differential parameters in the rows of compounds **10, 14, 15.**

Absolute values of $\Delta\delta_0^H$ differential parameters.

It should be noted that the value of $\Delta\delta_0^{H,N(n)}$ differential parameter monotonically decreases in the row **15a→15b→15c→15d** as hydrogen atoms are substituted by methyl groups. Such monotony is not preserved in the similar row of the compounds **14** (see Fig. 2). At first there is a little increase of $\Delta\delta_0^{H,14b}$ parameter (by 0.01 ppm) while

transition from **14a** to **14b**, then a zero change while transition to **14c** and a sharp decrease of $\Delta\delta_0^{H,N(n)}$ parameter to –0.26 ppm while transition to **14d**.

Let us note that the absolute values of the change of $\Delta\delta_0^{H,N(n)}$ parameter (which we denote as new differential parameter: $\left|\Delta\Delta\delta_0^H\right|$) are the same and equal to the assumed experimental error of 0.02 ppm for the first two steps (**15a→15b** and **15b →15c**) in the row of unsubstituted compounds **15** (where X, Y=H, CH_3. For the third step **15c→15d** the value of $\left|\Delta\Delta\delta_0^H\right|$ is practically the same (0.03 ppm), especially that δ_0^H parameters were taken from different sources [2] and [3].

The absolutely another situation takes place in the row of ketones **14a→14b→14c→14d.** For the first two steps of the row (**14a→14b** and **14b →14c**) the $\left|\Delta\Delta\delta_0^H\right|$ parameter is even less than experimental error. But for the last step (**14c→14d**) it increases sharply to 0.27 ppm. It means that changes of $\Delta\delta_0^{H,N(n)}$ parameter are different in two rows, i.e. they are monotonic for **15** and spasmodic for **14**.

Let us accentuate the considerable decrease of $\Delta\delta_0^{H,N(n)}$ parameter in the compounds of the B type while transition from the first to the last term of the row. Its absolute value we denote as new differential parameter $\left|\Delta\Delta\delta_0^{H,max}\right|$. Thus, while **15a→15d** transition this value is small ($\left|\Delta\Delta\delta_0^{H,max}\right| = 0.07$ ppm). At the same time it is greater while **14a→14d** transition ($\left|\Delta\Delta\delta_0^{H,max}\right| = 0.26$ ppm). Such value is comparable with the value of $\left|\Delta\Delta\delta_0^{H,max}\right| = 0.18$ ppm for styrenes **10** and it is greater than $\left|\Delta\Delta\delta_0^{H,max}\right| = 0.245$ ppm for the compounds **1** of A type. Moreover, we came to conclusion that $\left|\Delta\Delta\delta_0^{H,max}\right|$ values for the other compounds of the series A (**2, 4, 5, 6**) and B (**9**) may be in the range from 0.05 to 0.20 ppm. Thus in all rows of investigated compounds A and B types there is an essential change (increase or decrease) of basic spectral parameter $\delta_0^{H,N(n)}$ while transition from the first to the last term of the row.

IV.   Conclusions.

The **new regular "structure-property" dependencies** which were determined earlier [1] for nonfunctionalized monoalkylbenzenes **1** and **15-17** are observed for all values of basic spectral parameters $\delta_0^{H,N(n)}$ in the investigated rows of monoalkylbenzenes substituted by functional substituents in the side chain. **α- and β-Effects** (change of chemical shift of ortho-protons δ_0^H in NMR ${}^1H$ spectra) are used as "property" and **changes of saturation of definite spatial areas** by methyl groups near phenyl ring are used as "structure". It should be stressed that for the investigated compounds **1-17 there are no facts contradicting** with the existing of "α-effect" at the branching of alkyl chain near α-carbon atom and "β-effect" observed at the branching near β-carbon atom.

In spite of the fact that above-mentioned data are insufficient for the acceptance of universal action of α- and β-effects in the case of bulky substituents near phenyl ring in monosubstituted benzenes and following investigations would be desirable (including the determination of application area of mentioned effects), **we may state** with confidence that **postulated regularities "structure-property" are actual for both unsubstituted and substituted** by functional groups in the side chain **monoalkylbenzenes**.

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