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EFFECT OF SUBSTITUENT GEOMETRICAL PARAMETERS ON THE CHEMICAL SHIFTS OF ORTHO- AND META-PROTONES IN NMR ^{1}H SPECTRA OF MONOSUBSTITUTED BENZENES

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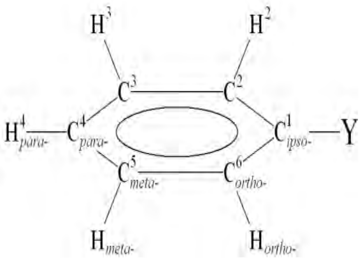
Abstract. Spectral (NMR ^{1}H) parameters of phenyl ring protons in 26 monosubstituted benzenes C_6H_5-*Y*, including benzene, have been investigated. The values of *ortho*-, *meta*- and *para*-protons chemical shifts, as well as differences between the values of mentioned protons absorption have been analyzed by analytical and graphical ways. The concept of ideal plots for three types of phenyl protons and substituent "voluminosity" has been introduced. The dependence of voluminosity on substituent chemical structure and influence of voluminosity on the chemical shift of ortho-protons signals were shown. The plots of *ortho*-protons chemical shifts *versus* Brown constants have the high (99 % and more) correlation coefficient.

Keywords: NMR ^{1}H spectra, monosubstituted benzenes, chemical shift, proton, Brown constant.

1. Introduction

In our previous report [1] we presented the experimental results of the systematic investigations concerning the dependence between spectral parameters of the simplest aliphatic compounds – linear aliphatic molecules, containing functional end-group *Y* and their structure. The next step was to investigate *all spectral changes* occurring in NMR ^{1}H and ^{13}C spectra in the simplest aromatic compounds – *monosubstituted benzene derivatives* which are formed while introducing various substituents *Y* in the molecule of the reference substance – benzene.

Earlier [2] we described the dependence of phenyl protons chemical shifts $d_i^{H,N}$ in NMR ^{1}H spectra of monosubstituted benzenes (1–26) on the parameters characterizing the nature of *Y* substituent in definite chemical reactions, for example on Hammett constants *s* or Brown constants s^+, *etc*. We analyzed 66 equations of $d_i^{H,N}$ dependencies (by 22 for every of three types of phenyl ring protons, *i.e.* *i* = *o*-, *m*-, *p*-) in 25 monosubstituted benzenes (**1–11** and **13–26**) of the general formula C_6H_5-*Y*. Benzenes contain 25 the most widespread substituents *Y* and non-substituted benzene **12**[1]. The best correlation coefficient (0.966) was found for the dependence ($\Delta d_p^{H,N}-s^*$), *i.e.* for the dependence of *para*-protons chemical shifts on Brown *para*-constants s^+. Factors affecting the values of linear correlation coefficients are examined in [3]. In this work we use the same 26 monosubstituted benzenes **1–26** (including the non-substituted benzene **12**, *Y* = H).



where *Y* = N(CH_3)$_2$ (**1**), NH_2 (**2**), OH (**3**), OCH_3 (**4**), OC_6H_5 (**5**), SCH_3 (**6**), CH_3 (**7**), C_2H_5 (**8**), *i*-C_3H_7 (**9**), *t*-C_4H_9 (**10**), C_6H_5 (**11**), H (**12**), Si(CH_3)$_3$ (**13**), F (**14**), Cl (**15**), Br (**16**), I (**17**), CO_2H (**18**), CO_2CH_3 (**19**), $CO_2C_2H_5$ (**20**), CF_3 (**21**), CH_3C=O (**22**), CH=O (**23**), CN (**24**), SO_2CH_3 (**25**), NO_2 (**26**)

2. Experimental

Table 1 represents the literature data of aromatic protons chemical shifts $\delta_i^{H,N}$, which we considered to be "basic spectral parameters" (BSP). For the convenience here we introduce the contracted notations allowing to

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[1] The choice of Y substituents is conditioned by the presence of maximum amount of table "constants" – parameters characterizing the substituent nature; the numbering scheme coincides mainly with the increase in value of their Brown constants s^+.

refuse subscripts and superscripts and to simplify symbols. In every case the new symbol is doubled by the previous one. Thus the value of chemical shift for aromatic proton of ***i*** type (*i* = *o*-, *m*-, *p*-) in the compound **N**, *i.e.* parameter $\delta_i^{H,N}$**,** we denote as *N-B-i*. For example, symbol **10**-*B-o* = 7.39 ppm denotes the chemical shift of *ortho*-protons in *tert*-butylbenzene **10.** Its previous designation was $\delta_o^{H,\mathbf{10}}$ = 7.39 ppm. The capital letter *B* in the above mentioned symbols distinguishes them from differential spectral parameters *N-D-i*.

The choice of literature sources was grounded on the observation of their reliability and compatibility. We used only *N-B-i* values obtained in deuterochloroform as a solvent and described in the reference books [4, 5]. Here we do not examine spectra obtained in other solvent, ***e.g.*** DMSO-d6. The parameters *N-B-i* given in [4] were obtained using instruments with different frequencies: low-frequency (90 MHz) and high-frequency (300 or 400 MHz). "Low-frequency" parameter was used only in the absence of "high-frequency" value. The authors of data represented in [4] give their own attribution of spectra signals to the absorption of definite types of hydrogen atom nuclei. The authors of data represented in [5] do not give their own attribution of spectra signals; therefore we do this by ourselves.

For obviousness and convenient calculations the values of differential spectral parameters *N-D-i* denoted previously as $\Delta\delta_i^{H,N}$ are given in Table 1. *N-D-i* is the chemical shift calculated relative to non-substituted benzene **12.** They are calculated for each of three types protons for all compounds **1**–**26** according to the formula: $\Delta\delta_i^{H,N} = \delta_i^{H,N} - \delta_i^{H,\mathbf{12}}$ (or *N-D-i* = *N-B-i - 12-B-i*). Values of *N-D-i* are always with "+" or "–" and it is advisable to express them in the milliardth parts (mlrd**.**) on the basis of 1 ppm = 1000 mlrd**.** Table 1 also represents other differential parameters denoted as *N-(o-m)* and *N-(m-p)* discussed below. We estimate the inaccuracy of measurements as ± 0.02 ppm (20 mlrd**.**). All values of basic spectral parameters *N-B-i* of compounds **1**–**26** were taken without changes from [2], but rounded to the nearest number divisible by 0.01 ppm (10 mlrd**.**)

Table 1

Values of basic (*N-B-i* or $\delta_i^{H,N}$), differential (*N-D-i* or $\Delta\delta_i^{H,N}$), *N-(o-m)* = $\Delta\delta_{o\text{-}m}^{H,N}$, and *N-(m-p)* = $\Delta\delta_{m\text{-}p}^{H,N}$ spectral parameters for the compounds 1–26

No.	Substituent *Y*	*N-B-i* ($\delta_i^{H,N}$), ppm			*N-D-i* ($\Delta\delta_i^{H,N}$), mlrd.			*N-(o-m)* ($\Delta\delta_{o\text{-}m}^{H,N}$) and *N-(m-p)* ($\Delta\delta_{m\text{-}p}^{H,N}$), mlrd.	
		N-B-o δ_o^H	*N-B-m* δ_m^H	*N-B-p* δ_p^H	*N-D-o* $\Delta\delta_o^H$	*N-D-m* $\Delta\delta_m^H$	*N-D-p* $\Delta\delta_p^H$	*N-(o-m)* $\Delta\delta_{o\text{-}m}^{H,N}$	*N-(m-p)* $\Delta\delta_{m\text{-}p}^{H,N}$
1	NMe_2	6.73	7.23	6.71	−600	−100	−620	-500	+520
2	NH_2	6.63	7.13	6.73	−700	−200	−600	-500	+400
3	OH	6.82	7.22	6.92	−510	−110	−410	-400	+300
4	OMe	6.89	7.27	6.93	−440	−60	−400	-380	+340
5	OPh	7.00	7.30	7.07	−330	−30	−260	-300	+230
6	SMe	7.25	7.25	7.11	−80	−80	−220	0	+140
7	Me	7.15	7.23	7.14	−180	−100	−190	-70	+90
8	Et	7.18	7.26	7.15	−150	−70	−180	-80	+110
9	i-Pr	7.22	7.27	7.15	−110	−60	−180	-50	+120
10	t-Bu	7.39	7.29	7.16	+60	−40	−170	+100	+140
11	Ph	7.57	7.40	7.31	+240	+70	−20	+170	+90
12	H	7.33	7.33	7.33	0	0	0	0	0
13	$SiMe_3$	7.52	7.33	7.33	+190	0	0	+190	0
14	F	7.03	7.31	7.10	−300	−20	−230	-280	+210
15	Cl	7.32	7.26	7.21	−10	−70	−120	+60	+50
16	Br	7.48	7.20	7.26	+150	−130	−70	+280	-60
17	I	7.68	7.07	7.30	+350	−260	−30	+610	-230
18	CO_2H	8.13	7.46	7.60	+800	+130	+270	+670	-140
19	CO_2Me	8.04	7.42	7.53	+710	+90	+200	+620	-110
20	CO_2Et	8.05	7.42	7.53	+720	+90	+200	+630	-110
21	CF_3	7.61	7.46	7.53	+280	+130	+200	+150	-70
22	Ac	7.95	7.44	7.55	+620	+110	+220	+510	-110
23	CH=O	7.87	7.52	7.62	+540	+190	+290	+350	-100
24	CN	7.65	7.47	7.61	+320	+140	+280	+180	-140
25	SO_2Me	7.95	7.58	7.67	+620	+250	+340	+370	-90
26	NO_2	8.22	7.56	7.71	+890	+230	+380	+660	-150

3. Results and Discussion

3.1. Graphic Interpretation of NMR ^{1}H Spectral Parameters of Monosubstituted Benzenes

To our mind, the visual demonstration of *N-D-i* differential values ratio is the best on the plots for each of all 26 compounds. The most suitable plot is the dependence of *N-D-i* value on a number of chemical bonds (*n*) between the substituent *Y* and investigated proton. It depicts the change in values *DSP* of the compound *N* for protons of aromatic hydrogen atoms ***i*** gradually as their distance from the substituent increases, *i.e.* for *ortho* → *meta* → *para*-protons.

3.1.1. Plot structure

The number of chemical bonds ***n*** between the substituent *Y* and *ortho*-H is equal to three: the first one is the bond between the substituent *Y* and carbon atom C_{ipso}; the second one is C_{ipso}-C_{ortho} and the third one is C_{ortho}-H_{ortho}. The number of bonds is 4 for *meta*-protons and 5 – for *para*-protons. Hence, *n* = 3, 4 and 5 are plotted at abscissa and the diagram starts from *n* = 3. The point *N-D-o* has the following coordinates: abscissa is 3.00 and ordinate is *N-D-o* value in mlrd. The point *N-D-m* has the following coordinates: abscissa is 4.00 and ordinate is *N-D-m* value in mlrd. Connecting these two points by straight vector we obtained the left branch of the plot. The right branch of the plot is constructed in the same way by connection of *N-D-m* point (*n* = 4) and *N-D-p* point (*n* = 5).

The projection of the left branch on the ordinate axis is also the vector because it has the direction (as a consequence, sign "+" or "–"). It is equal to the new differential spectral parameter given in Table 1 and denoted as *N*-(*o-m*). This parameter is a difference between basic spectral parameters: *N-(o-m)* = *N-B-o* – –*N-B-m* (or $\Delta\delta_{o-m}^{H,N} = \delta_o^{H,N} - \delta_m^{H,N}$). It may be also represented as the difference between differential parameters *N-D-i*: *N-(o-m)* = *N-D-o* – *N-D-m* (or $\Delta\delta_{o-m}^{H,N} = \Delta\delta_o^{H,N} - \Delta\delta_m^{H,N}$). Therefore the central letter ***B*** or ***D*** is absent. In the same way we denote the projection of the right branch by differential parameter *N-(m-p)* = *N-B-m* – *N-B-m.*

Every branch of the plot may be "steep", "flat" or parallel to abscissa. The line steepness is a qualitative value[2] but depends on absolute values of parameters |*N-(o-m)*| for the left and |*N-(m-p)*| for the right branch. The larger value, the steeper is the slope angle.

3.1.2. Plot types

While varying different signs of differential parameters *N*-(*o-m*) and *N*-(*m-p*) four types of plots are possible. Three of them are depicted in Figs. 1-3. Figs. 1 and 2 represent the variant when *N*-(*o-m*) and *N*-(*m-p*) parameters have different signs. Every branch of the plots is situated in one of two "right" quadrants: in the first or forth one. Thus on the plot 1 (parameter *N*-(*o-m*) < 0, and parameter *N*-(*m-p*) > 0) the left branch is situated in the first quadrant and the right one – in the forth quadrant (Fig. 1). The plot 2 (Fig. 2) is for the opposite case, when *N*-(*o-m*) > 0, *N*-(*m-p*) < 0. Thus its left branch is situated in the forth quadrant and the right one – in the first quadrant.

Fig. 3 represents the case when *N*-(*o-m*) and *N*-(*m-p*) have the same sign, in our case – sign "plus" (*N*-(*o-m*) > 0 and *N*-(*m-p*) > 0). Both branches of the plot are situated in the forth quadrant. The variant when both parameters are less than zero is not represented in Figs., because it does not occur in practice.

If one of the parameters *N*-(*o-m*) and *N*-(*m-p*) is equal to zero, we obtain other four types of plots (two of them are represented in Figs. 4 and 5 and the rest two do not occur in practice). Fig. 4 represents the case when *N*-(*o-m*) = 0 and *N*-(*m-p*) < 0; Fig. 5 – when *N*-(*o-m*) > 0 and *N*-(*m-p*) = 0. The ninth type represents the case when both parameters are equal to zero, therefore both branches of the plot are situated on abscissa. It is the plot for benzene **12** (*Y* = H) which is called "zero line" or "benzene line" because all three parameters *N-B-i* are equal to 7.33 ppm (*i.e. N-D-i* is equal to 0 mlrd.). Hence, *N*-(*o-m*) = *N*-(*m-p*) = 0 mlrd. The plots for the rest 25 compounds are broken lines consisted of two slanting branches. They cross in the point determined by the chemical shift of *meta*-protons (*n* = 4). Every plot corresponds to one of eight types discussed above and represented in Figs. 1–5.

The plots of the majority of benzene compounds (including benzene **12** as itself) are represented in Fig. 6. The most of the plots (18 from 25) correspond to the first two types, that is why we consider them as typical plots.

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[2] The scale of dimensionless value is arbitrary. Thus the pace between two nearest points *n* along abscissa which are divisible by 1, *e.g.* between *n* = 3.00 (*ortho*-) and *n* = 4.00 (*meta*-), is a random value and depends only on the authors preference. Therefore the slope angle of every branch to abscissa has no physical sense and is not calculated.

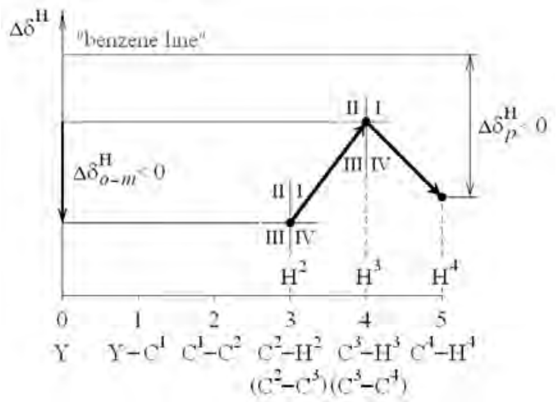

Fig. 1. Plot of the type 1 (N-(o-m) < 0, N-(m-p) > 0

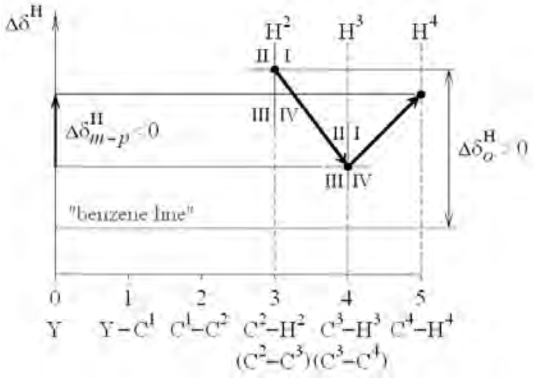

Fig. 2. Plot of the type 2 N-(o-m) > 0, N-(m-p) < 0

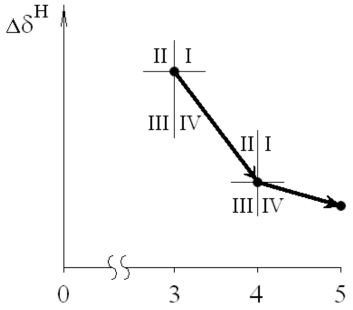

Fig. 3. Plot of the type 3 (N-(o-m) > 0 and N-(m-p) > 0)

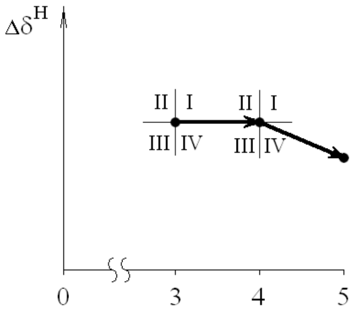

Fig. 4. Plot of the type 4 (N-(o-m) = 0 and N-(m-p) < 0)

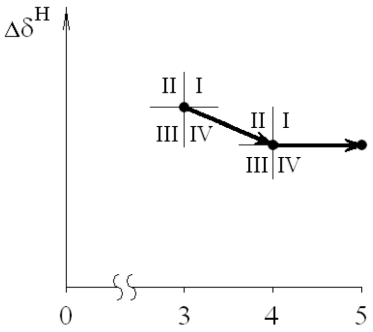

Fig. 5. Plot of the type 5 (N-(o-m) > 0 and N-(m-p) = 0)

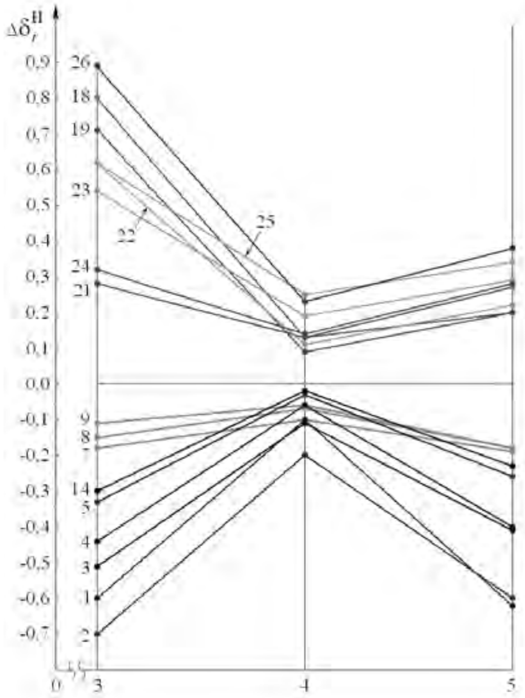

Fig. 6. Graphic interpretation of “real” spectral parameters N-(o-m) and N-(m-p) for 18 of 26 monosubstituted benzenes N (*Table 1*)

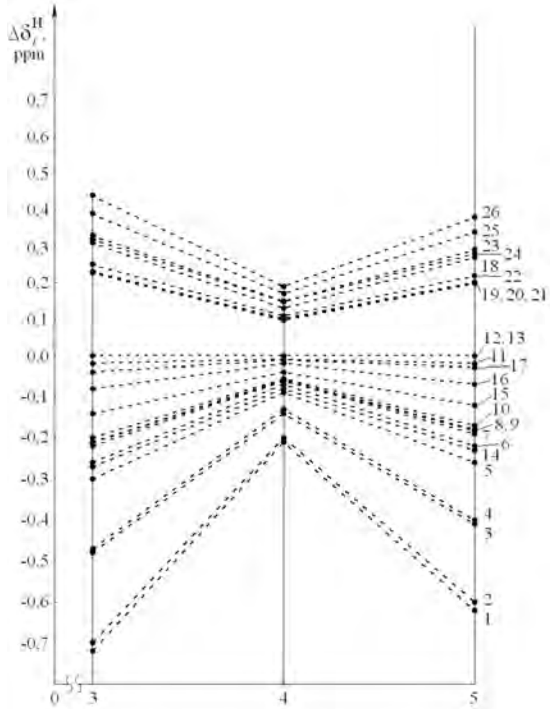

Fig. 7. Graphic interpretation of “ideal” spectral parameters Npr-(o-m) and Npr-(m-p) for 26 monosubstituted benzenes N (*Table 2*)

3.1.3. Plots of the compounds 1-11 containing electron-donor substituents

For the majority of compounds with electron-donor substituents Y (1-11)[3] the typical plot corresponds to the first type represented in Fig. 1. For the compounds **1** [$Y = N(CH_3)_2$] and **2** ($Y = NH_2$) containing aminogroups as substituents with the most strong electron-donor properties, we obtain the plots with the most steep branches. They are depicted in the bottom part of Fig. 6. The absolute values of their parameters *N*-(*o-m*) and *N*-(*m-p*) are equal to 400–500 mlrd. The plots of phenol **3**, its ethers **4** and **5,** fluorobenzene **14** are situated higher than those of the compounds **1** and **2** (Fig. 6). The compounds **3–5** and **14** contain the weaker electron donor substituents (OR or F) compared with aminogroups. Their absolute values *N*-(*o-m*) and *N*-(*m-p*) are less and equal to 200–400 mlrd. Therefore, both branches of these plots are flatter compared with the plots of compounds **1** and **2**. The plots of three "transitional compounds" – alkylbenzenes: toluene **7**, ethylbenzene **8** and cumene **9** are situated in the upper part of Fig. 6 near the "benzene line". They contain "medium" by strength electron-donor alkyl groups as the substituents *Y*. Both branches are even flatter because the absolute values of *N*-(*o-m*) and *N*-(*m-p*) parameters are small and equal to 50–100 mlrd. The plots of the rest three compounds (**6, 10** and **11**) are represented in Figs. 3 and 4.

3.1.4. Plots of the compounds 18–26 containing electron-acceptor substituents

The plots of monosubstituted benzenes with electron-acceptor substituents *Y* (**18–26**) are represented in the upper part of Fig. 6 and correspond to the second type (Fig. 2). Nitrobenzene **26** with the strongest electron-acceptor nitrogroup ($Y = NO_2$) is shown by the highest peak in Fig. 6. The same as for benzoic acid, the left branches are the steepest ones [|**18**-*(o-m)*| = 670 mlrd.] and |**26**-*(o-m)*| = 660 mlrd.

3.1.5. Typical plots

The plots with the steepest branches have the form of high hill (anilines **1** and **2**) or asymmetric deep pit (nitrobenzene **26**). The plots of "transitional" compounds have the same forms but they are flatter. All "pits" are situated above the "benzene line" and all "hills" – under it.

19 of 26 plots of monosubstituted benzenes (including non-substituted benzene) are represented in Fig. 6. All of them are similar to the typical plots represented in Figs. 1 and 2. The highest "hills" are observed for anilines **1** and **2** and the deepest "pit" – for nitrobenzene **26**. Moreover, the plot of nitrobenzene is the most asymmetric relative to a vertical passing through the point of ***meta***-protons (at $n = 4$): its left (descending) branch is steeper than its right (ascending) one [|***26**-(o-m)*| = = 660 mlrd.] *vs* [|***26**-(o-m)*| = 150 mlrd.]. At the same time the plots of anilines **1** and **2** are almost symmetric because the absolute values of their parameters are close (|*N-(o-m)*| = ≈500 mlrd. and |*N-(m-p)*| = ≈ 400–500 mlrd.).

3.1.6. Atypical plots

In three of 7 atypical plots (where $Y = Bu^t$ (**10**), Ph (**11**) and Cl(**15**)) both branches are slanting. But there is no transition from one quadrant to another in the cross point. In all three cases the parameters *N*-(*o-m*) and *N*-(*m-p*) have the same sign "+", *i.e.* *N*-(*o-m*) > 0 and *N*-(*m-p*) > 0.Therefore both branches of the plot are situated in the forth quadrant and correspond to the type represented in Fig. 3. In two of 4 other atypical plots one of the branches is parallel to abscissa (the left branch in thioanizole **6** and the right one in phenyltrimethylsilane **13**). They correspond to the types represented in Figs. 4 and 5.

The rest two plots belong to haloidbenzenes (Y = Br (**16**) and Y = I (**17**)) and do not correspond to any of 9 types. They are discussed in [6]. Both plots are similar to the "pit" of nitrobenzene **26** (Fig. 2) but they are deeper. The cross point ($n = 4$) is situated below the "benzene line". The deepest "pit" is observed for iodbenzene **17**.

3.2. Analysis of Plots for the Compounds 1–26

Let us consider in details the quantitative ratio of every branch projection on the ordinate axis, *i.e.* parameters *N*-(*o-m*) and *N*-(*m-p*).

3.2.1. Virtual plots

While moving bottom-up from the "steep hills" (anilines **1** and **2** plots) to the "plain" of neutral benzene **12** (Fig. 6) the gradual flattening of the next "hill-knoll" is observed. At the last stage we observe the transformation of the "low knoll" (cumene **9**) into the "plain" one for benzene **12**. At the same time the plots likeness is preserved.

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[3] We relate trimethylsilyl group [$Y = Si(CH_3)_3$] in trimethylphenylsilane **13** neither to electron-donor nor to electron-acceptor substituents because its constants characterizing the substituent do not significantly differ from zero but have different signs (Hammet constant has "+" and Brown constant has "–"). Three differential parameters of the compound **13** are equal to zero (**13**-*D-m* = **13**-*D-p* = **13**-(*m-p)* = 0). Therefore the "ideal plot" of the compound **13** (given in Fig. 7) coincides with the "benzene line", *i.e.* "zero line".

It should be noted that while moving from the plot situated in the bottom of Fig. 6 to the plot in the upper part the gradual decrease of the absolute negative value of each of three parameters *N-D-i* takes place with different rate for every parameter. Actually sometimes one or two branches of the plots cross due to the disproportional change (increase or decrease) of *N-D-o* and *N-D-m* parameters (*vide* the left branches of dimethylaniline **1** and phenol **3** or the right branches of dimethylaniline **1** and aniline **2**).

3.2.1.1. "Ideal" plots of the compounds 1–11 with electron-donor substituents *Y*

Let us consider the ideal case when the proportions of *N-D-i* parameters change of every plot would be preserved at the step-by-step transition from the "high hill" (aniline **2**) to the "low knoll" (cumene **9**). We denote these parameters as "ideal proportional" differential parameters *Npr-D-i* ($\Delta d_{i,pr}^{H,N}$). We accept the values of *para*-protons *N-D-p* "real" (experimental) parameters given in Table 1 as a constant basis, *i.e.* we accept that *N-D-p = Npr-D-p.* We call these parameters "ideal proportional" *para*-parameters. The reason for such choice was the fact that *N-D-p* linear correlation coefficient from Brown *para*-constants was found to be the best just for *para*-parameters. Then in order to preserve the proportions at every step of transition the expected decrease of absolute value (negative by sign) of "ideal proportional" parameters *Npr-D-o* and *Npr-D-m* should be proportional to the decrease of "ideal proportional" parameter *Npr-D-p*, *i.e.* real parameter *N-D-p*. It means that virtual parameters *Npr-D-i* are calculated just for such ideal cases when the values of chemical shifts of *ortho*- and *meta*- protons would be proportional to the values of *para*-protons chemical shifts for all monosubstituted benzenes **1–26**.

Obviously the greatest changes of the absolute value take place for *ortho*-parameters *Npr-D-o*. For *meta*-parameters *Npr-D-m* these changes are the least and they are medium for "ideal proportional" *para*-parameters *Npr-D-p = N-D-p*. Therefore with every step toward the "benzene line" every next "ideal plot" becomes flatter. At the same time the branches of adjoining "ideal plots" do not cross and the likeness of plots is preserved as far as possible (Fig. 7).

3.2.1.2. Coefficients of proportionality used for the calculations of "ideal proportional" parameters *Npr-D-o* and *Npr-D-m* in the compounds 1-11

We denote the coefficient of proportionality of "ideal proportional" parameters *Npr-D-o* or *Npr-D-m* of *N* compound with the electron-donor substituent *Y* (*N* = **1**–**11**) as k_N equal to the ratio between its *para*-parameter *Npr-D-p = N-D-p* and analogical parameter *etal-D-p* of the reference compound chosen specially for this purpose. As the etalon it is advisable to choose the compound with an extreme value (in our case – minimum and maximum by absolute value) of *N-D-p* parameter so that all values of coefficient k_N would be less than one. In such a case the value k_N may be considered as qualitative characteristics of the substituent *Y* electron-donor strength.

We chose aniline **2** as the reference compound. The reasons for such choice are given below. The value *2-D-p* = -600 mlrd. is the second minimal values of *para*-parameters *N-D-p = Npr-D-p.* Then the coefficient k_N for cumene **9** (as an example) is equal to: k_9 = -180/(-600) = = 0.30. To preserve the likeness of "ideal plots" the parameters *Npr-D-o* and *Npr-D-m* are calculated in accordance to the formula: *Npr-D-i* = k_N·*etal.pr-D-i.*

For cumene **9** (Table 2) they are the following: for *ortho*-H: **9***pr-D-o* = 0.30·(-700) = -210 mlrd.; for *meta*-H: **9***pr-D-m* = 0.30·(-200) = -60 mlrd. For only one compound – N,N-dimethylaniline**1** [*Y* = $N(CH_3)_2$] – the coefficient of proportionality is higher than one and equals to: k_1 = (-620)/(-600) ≈1.03, and **1***pr-D-o* = 1.03·(-700) = = -720 mlrd.

3.2.1.3. Virtual "basic proportional" parameters *Npr-B-o* and *Npr-B-m* in the compounds 1-11.

Let us introduce the conception of virtual basic proportional parameters and note them as *Npr-B-o* and *Npr-B-m.* They are equal to the algebraic sum of benzene protons chemical shift and proportional differential parameters *Npr-D-o* and *Npr-D-m*. Hence: *Npr-B-o* = = 7.33 ppm + *Npr-D-o* (or 7.33 ppm + $\Delta d_{o,pr}^{H,N}$); and *Npr-B-m* = 7.33 ppm + *Npr-D-m* (or 7.33 ppm + + $\Delta d_{m,pr}^{H,N}$). For cumene **9** taken as an example, we obtained the following calculated "virtual" values of basic proportional parameters (Table 2): **9***pr-B-o* = 7.33 ppm – – 0.21 ppm = 7.12 ppm (instead of "real" value **9**-*B-o* = = 7.22 ppm; Table 1) and **9***pr-B-m* = 7.33 ppm – – 0.06 ppm = 7.27 ppm corresponded to the given in Table 1 the "real" value **9**-*D-m* = 7.27 ppm.

3.2.1.4. Virtual "basic proportional" parameters *Npr-B-o* and *Npr-B-m* in the compounds 18-26 containing electron-acceptor substituents *Y*

The same situation (but as a mirror reflection) should be for nine "typical" plots of the compounds with electron-attracting substituent *Y* (**18-26**) given in the upper part of Fig. 6. It means that during step-by-step transition from the top downward (from nitrobenzene **26** to benzene **12**) we observe the gradual "decrease of pit depth". The proportionality between calculated "basic proportional" parameters *Npr-B-o* and *Npr-B-m*, where (*N* = **18-26**), and constant *para*-parameters *Npr-D-p* = *N-D-p* is preserved. But to calculate the proportionality coefficient k_N we use benzonitrile **24** as a reference compound. The reasons for exchange of nitrobenzene **26** with the maximum parameter **26**-*D-p* = +380mlrd. for benzonitrile **24** (*etal-D-p* = **24**-*D-p* = +280 mlrd.) are given below. In such a case the coefficients of three compounds (**23, 25** and **26**) are greater than one (Table 2).

3.2.1.5. Reasons for the reference compounds choice

The choice of aniline **2** as the reference compound for **1-11** with electron-releasing groups *Y* instead of *para*-N,N-dimethylaniline **1** with the extreme parameter **1**-*D-p* = -620 mlrd. is caused by the fact that aniline **2** has extreme (minimal) values of *ortho*-protons (**2**-*D-o* = -700 mlrd. and **1**-*D-o* = -600 mlrd.) and *meta*-parameters (**2**-*D-m* = -200 mlrd. and **1**-*D-m* = -100 mlrd., see Table 1). At the same time the values of *para*-parameters **1** and **2** are similar to each other (**1**-*D-p* = -620 mlrd., and **2**-*D-p* = -600 mlrd.). Moreover, it is important that the left branch of the reference compound plot (as for the majority of **1-11**) should be negligibly steeper than the right one. This requirement is fulfilled for aniline **2** because |**2**-*(o-m)*| = = 505 mlrd., and |**2**-*(m-p)*| = 400 mlrd.; their ratio is |**2**-*(o-m)*| / |**2**-*(m-p)* | ≈ 1.26. For the similar parameters of the compound **1** (|**1**-*(o-m)*| = 505mlrd., and |**1**-*(m-p)* | = = 520 mlrd**.**) their ratio is less than one (≈ 0.97). It means that the right branch is steeper than the left one.

Taking into account all above-mentioned we choose benzonitrile **24** as the reference compound to calculate coefficients k_N for **18-26**. Its plot is symmetric in contrast to the asymmetric plot of nitrobenzene **26**.

Table 2

Values of the coefficients of proportionality k_N; experimental basic spectral parameters *N-B-i* ($d_i^{H,N}$); virtual "basic proportional" parameters *Npr-B-i* ($d_{i,pr}^{H,N}$); their differences D*N-B-i* and "differential proportional" parameters *Npr-D-i* (D$d_{i,pr}^{H,N}$) for all types of "*i*" protons in NMR spectra of monosubstituted benzenes 1-26

N	Substituent *Y*	*Para*-protons		*Ortho*-protons				*Meta*-protons			
		N-D-p = = *Npr-D-p* = = $d_p^{H,N}$, ppm	k_N	*N-B-o* = = $d_o^{H,N}$, ppm	*Npr-D-o* = = $\Delta d_{o,pr.}^{H,N}$, mlrd.	*Npr-B-o* = = $d_{o,pr.}^{H,N}$, ppm	Δ*N-B-o*, mlrd.	*N-B-m* = = $d_m^{H,N}$, ppm	*Npr-D-m* = = $\Delta d_{m,pr.}^{H,N}$, mlrd.	*Npr-B-m* = = $d_{m,pr.}^{H,N}$, ppm	Δ*N-B-m*, mlrd.
1	NMe_2	**6.71**	1.03	**6.73**	-720	***6.61***	*+120*	**7.23**	-210	***7.12***	*+110*
2	NH_2	**6.73**	1.00	**6.63**	−700	***6.63***	*0.00*	**7.13**	−200	***7.13***	*0*
3	OH	**6.92**	0.68	**6.82**	-480	***6.85***	***-30***	**7.22**	-140	***7.19***	*+30*
4	OMe	**6.93**	0.67	**6.89**	-470	***6.86***	*+30*	**7.27**	-130	***7.20***	*+70*
5	OPh	**7.07**	0.43	**7.00**	-300	***7.03***	*+30*	**7.30**	-90	***7.24***	*+60*
6	SMe	**7.11**	0.37	**7.25**	−260	***7.07***	*+180*	**7.25**	−70	***7.26***	***-10***
7	Me	**7.14**	0.32	**7.15**	−220	***7.11***	*+40*	**7.23**	−60	***7.27***	***-40***
8	Et	**7.15**	0.30	**7.18**	−210	***7.12***	*+60*	**7.26**	−60	***7.27***	***-10***
9	i-Pr	**7.15**	0.30	**7.22**	−210	***7.12***	*+100*	**7.27**	−60	***7.27***	*0*
10	t-Bu	**7.16**	0.28	**7.39**	−200	***7.13***	*+260*	**7.29**	−60	***7.27***	*+20*
11	Ph	**7.31**	0.03	**7.57**	−20	***7.31***	*+260*	**7.40**	−10	***7.32***	*+80*
12	H	**7.33**	0.00	**7.33**	0	***7.33***	*0*	**7.33**	0	***7.33***	*0*
13	$SiMe_3$	**7.33**	0.00	**7.52**	0	***7.33***	*+190*	**7.33**	0	***7.33***	*0*
14	F	**7.10**	0.38	**7.03**	−270	***7.06***	*−30*	**7.31**	−80	***7.25***	*+60*
15	Cl	**7.21**	0.20	**7.32**	−140	***7.19***	*+130*	**7.26**	−40	***7.29***	***-30***
16	Br	**7.26**	0.12	**7.48**	−80	***7.25***	*+230*	**7.20**	−20	***7.31***	***-110***
17	I	**7.30**	0.05	**7.68**	−40	***7.29***	*+390*	**7.07**	−10	***7.32***	***-250***
18	CO_2H	**7.60**	0.96	**8.13**	+310	***7.64***	*+490*	**7.46**	+130	***7.46***	*0*
19	CO_2Me	**7.53**	0.71	**8.04**	+230	***7.56***	*+480*	**7.42**	+100	***7.43***	***-10***
20	CO_2Et	**7.53**	0.71	**8.05**	+230	***7.56***	*+490*	**7.42**	+100	***7.43***	***-10***
21	CF_3	**7.53**	0.71	**7.61**	+230	***7.56***	*+50*	**7.46**	+100	***7.43***	*+30*
22	Ac	**7.55**	0.79	**7.95**	+250	***7.58***	*+370*	**7.44**	+110	***7.44***	*0*
23	CH=O	**7.62**	+1.04	**7.87**	+330	***7.66***	*+210*	**7.52**	+150	***7.48***	*+40*
24	CN	**7.61**	1.00	**7.65**	320	***7.65***	*0*	**7.47**	+140	***7.47***	*0*
25	SO_2Me	**7.67**	+1.21	**7.95**	+390	***7.72***	*+230*	**7.58**	+170	***7.50***	*+80*
26	NO_2	**7.71**	1.36	**8.22**	440	***7.77***	*+450*	**7.56**	190	***7.52***	*+40*

The plots of aniline **2** and benzonitrile **24** have virtually the same and high degree of symmetry: |**2**-*(o-m)*| / |**2**-*(m-p)*| ≈ 1.26, and ratio |**24**-*(o-m)*| / |**24**-*(m-p)*| = = 0.18/0.14 ≈ 1.29. These proportions are preserved while constructing "ideal proportional" plots for all 26 monosubstituted benzenes with both types of substituent *Y* given in Fig. 7. For the contrast we compare them with above-mentioned data for the most asymmetric "real" plot of nitrobenzene **26** where ratio |**26**-*(o-m)*| / / |**26**-*(m-p)*| = 660/150 = 4.40, *i.e.* the left branch is significantly steeper than the right one.

3.2.1.6. Calculations of virtual parameters

Table 2 presents: a) calculated dimensionless values of the coefficient of proportionality k_N; b) values of virtual chemical shifts of *ortho*-(*Npr-B-o*) and *meta*-protons (*Npr-B-m*) for each of 26 compounds given in ppm and designated by italic bold; c) proportional differential parameters *Npr-D-o* and *Npr-D-m* given in mlrd; d) the differences between the real value of parameters $d_i^{H,N}$ and their calculated "proportional" values $d_{i,pr}^{H,N}$ designated by italic as Δ*N-B-i*, *i.e.* Δ*N-B-i* = = *N-B-i* – *Npr-D-i*; e) experimental values of basic spectral parameters *N-B-i* ($d_i^{H,N}$) taken from Table 1 and given here for the comparison designated by bold.

3.2.1.7. Virtual plots construction

The construction of "ideal" plot is advisable to start from its right branch. For this purpose real parameters of *para*-protons *N-D-p* (equal to the "proportional" parameters *Npr-D-p*) are taken from Table 1 and used as *para*-proton points (at *n* = 5). Virtual basic proportional parameters *Npr-D-m* are taken from Table 2 and used as *meta*-proton points (at *n* = 4). For the construction of the left branch it is necessary to use only virtual proportional parameters *Npr-D-o* and *Npr-D-m*. They provide relative "parallelism" (similarity) of both branches in the "ideal" plots.

For visualizing all 26 virtual "ideal" plots are located in Fig. 7. It should be stressed that "real" and "ideal" plots coincide **only** for the compounds **2** and **24**.

3.3. Main Differences of "Ideal Proportional" Plots from "Real" Plots for the Compounds 1-26

Among "real" plots of all 10 compounds with electron-releasing substituents *Y* (**1**, **3-11**) only two plots (compounds **3** and **7**) to our mind are close to the ideal form. For the compounds with electron-attracting substituents **18-23**, **25, 26** only one plot is close to the ideal form – the plot for (trifluoromethyl)toluene **21**. The most differing form has real plots of the compounds **1, 9, 18, 19, 25, 26** and especially **6, 10, 11** and **13**.

The form of the right branch of both "ideal" and "real" plots for each compound **1-26** is defined by the corresponding difference parameter that is discussed below. At first we analyze them and then compare "ideal" and "real" differential parameters which condition the form of the left branch.

3.3.1. Calculation of differential spectral parameters of every branch of virtual plots

To analyze the left and right branches of "real" plots we use "real" differential parameters *N-(o-m)* and *N-(m-p)*, respectively. These parameters are the projections of every branch of "real" plot on the ordinate axis. Similarly, while analyzing virtual "ideal" plots we use "ideal proportional" differential parameters, *Npr-(o-m)* ($\Delta d_{o\text{-}m,pr.}^{H,N}$) and *Npr-(m-p)* ($\Delta d_{m\text{-}p,pr.}^{H,N}$). By analogy with "real" difference parameters *N-(o-m)* and *N-(m-p)* we calculate them as the difference between "proportional" parameters in accordance with the formulas: *Npr-(o-m)* = *Npr-B-o* - *Npr-B-m* (or *Npr-(o-m)* = = *Npr-D-o* - *Npr-D-m*); and *Npr-(m-p)*= *Npr-D-m* - *N-D-p*. All values of monosubstituted benzenes **1-26** in mlrd. are given in Table 3. Additionally for each compound **1-26** we adduce the difference between the "real" parameter *N-(o-m)* [or *N-(m-p)*] and "ideal" parameter *Npr-(o-m)* [or *Npr-(m-p)*]. The difference is designated as Δ*N-(o-m)* and Δ*N-(m-p)* and calculated according to the formulas: Δ*N-(o-m)* = = *N-(o-m)* - *Npr-(o-m)* ($\Delta d_{o\text{-}m}^{H,N}$ - $\Delta d_{o\text{-}m,pr.}^{H,N}$); Δ*N-(m-p)* = = *N-(m-p)* - *Npr-(m-p)* ($\Delta d_{m\text{-}p}^{H,N}$ - $\Delta d_{m\text{-}p,pr.}^{H,N}$).

3.3.2. Analysis of the values of "proportional" differential spectral parameters ***Npr-(o-m)*** and ***Npr-(m-p)***

When comparing "ideal" and "real" plots of the compounds **1-13** and **18-26** (except haloidbenzenes **14-17** which were discussed earlier [6]) the regular differences are clearly observed. At first we discuss the right branch of the plot and then the left one.

It is advisable to discuss the right branch of the plots in reverse direction, *i.e.* from the right to the left (from *n* = 5 to *n* = 4). In such a case each of two plots of each compounds *N* starts from the same point with the following coordinates: abscissa *n* = 5; ordinate *N-D-p* = = *Npr-D-p* (or $\Delta d_p^{H,N}$ = $\Delta d_{p,pr}^{H,N}$, see above). Therefore the difference between the right branches of "real" and "ideal" plots is caused only by the difference between the values of "real and "ideal" *meta*-parameter (at *n* = 4) given in Table 2, *i.e.* Δ*N-(m-p)* = *N-D-m* – *Npr-D-m* = Δ*N-B-m*.

Table 3

Values of “ideal proportional” differential parameters *Npr-(o-m)* (D$d_{o\text{-}m,pr.}^{H,N} = d_{o,pr.}^{H,N} - d_{m,pr.}^{H,N}$) and *Npr-(m-p)* (D$d_{m\text{-}p,pr.}^{H,N} = d_{m,pr.}^{H,N} - d_{p,pr.}^{H,N}$), and their differences (D*N-(o-m)* and D*N-(m-p)*) on “real” parameters *N-(o-m)* and *N-(m-p)* in NMR spectra of monosubstituted benzenes 1-26

Parameter	Compound *N*												
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**
Npr-(m-p)	+410	+400	+270	+270	+170	+150	+130	+120	+120	+110	+10	0	0
D*N-(m-p)*	+110	0	+30	+70	+60	-10	-40	-10	0	+30	+80	0	0
Npr-(o-m)	-510	-500	-340	-340	-210	-190	-160	-150	-150	-140	-10	0	0
D*N-(o-m)*	+10	0	-60	-40	-90	+190	+90	+70	+100	+250	+180	0	+190

Parameter	Compound *N*												
	14	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**23**	**24**	**25**	**26**
Npr-(m-p)	+150	+80	+50	+20	-140	-100	-100	-100	-110	-140	-140	-170	-190
D*N-(m-p)*	+60	-30	-110	-250	0	-10	-10	+30	0	+40	0	+80	+40
Npr-(o-m)	-190	-100	-60	-30	+180	+130	+130	+130	+140	+180	+180	+220	+250
D*N-(o-m)*	-90	+160	+270	+640	+490	+490	+500	+20	+370	+170	0	+150	+410

The slope of the “real” plot right branch, *i.e.* its steepness is determined by the value of “real” differential parameter *N*-(*m-p*). Similarly, the steepness of the “ideal” plot right branch is determined by the value of “proportional” parameter *Npr*-(*m-p*). The difference between the steepness of every branch is determined by the value Δ*N*-(*m-p*) = Δ*N-B-m*.

For 22 monosubstituted benzenes (except 4 haloidbenzenes) the values Δ*N-B-m* of *meta*-parameters have both positive and negative meanings. It means that the right branch of “ideal” plot may be steeper or flatter than that of the “real” plot. However, the absolute values are similar (differ by no more than 40 mlrd.) resulting in slight difference between the slope of right branches. Only in 5 from 22 cases (including dimethylaniline **1**) the parameters Δ*N*-(*m-p*) are within the range from +60 to +110 mlrd. indicating more steeper direction of the right branch of the “real” plot compared with the “ideal” one.

Another situation is observed for the parameters *N*-(*o-m*) *and Npr*-(*o-m*) which determine the steepness of the left branches. We consider the left branch the same as the right one: from right to left. The left branches start from different points with the same abscissa (n = 4) but different ordinates. In the common case *N-D-m* ^{1} ^{1} *Npr-D-m.* Usually these ordinates differ by no more than 40 mlrd. excluding 5 cases mentioned above.

When analyzing “ideal” and “real” plots the most important are absolute values of *meta*-parameters *N-D-m* and *Npr-D-m* in the point with abscissa n = 4 which is common for both branches. If values |*N-D-m*| and |*Npr-D-m*| are larger compared with their difference, *i.e.* parameter |Δ*N-(m-p)*|, then the right branches of both plots will not significantly differ between each other relative to their steepness. Such situation takes place for “high hills” – plots of the compounds **1, 4, 5** and “deep pit” – compound **25,** when this exceeding is more than threefold (3·|Δ*N*-(*m-p*)| < |*N-D-m*| ≈ |*Npr-D-m*| > 3·|Δ*N-(m-p)*|). The form of the right branches slightly differs for them.

If the values |Δ*N*-(*m-p*)|, |*N-D-m*| and |*Npr-D-m*| are comparable between each other (for example for the plots “low knoll” or “shallow dip”), the large by absolute value parameter |Δ*N*-(*m-p*)|, which determines the steepness of the right branch, may essentially change the form of the “real” plot compared with the “ideal” one. The plots for toluene **7** and cumene **9** may be given as examples.

This diversity is the most evident in those cases when the second parameter |Δ*N*-(*o-m*)| which determines the steepness of the left branch has also the large absolute value. Very often in such cases the “real” plot changes unrecognizably. As an example we adduce the compounds **10** and especially **11** (Fig. 7). For example, for diphenyl **11** the right descending branch becomes very steep in the “real” plot instead of expected flat branch in the “ideal” plot due to the large value of parameter |Δ**11**-(*m-p*) = = Δ**11**-*B-m*|= 80 mlrd. compared with parameter |**11***pr*-(*m-p*)|= 10 mlrd. At the same time in the “real” plot the left branch transforms into a very steep descending branch instead of expected ascending flat branch in the “ideal” plot due to the large value of parameter |Δ**11***pr*-(*o-m*)| = = 180 mlrd. compared with parameter |**11***pr*-(*o-m*)| = = 10 mlrd. It means that the left branch transits from the expected first quadrant to the forth quadrant. That is why the plot of diphenyl **11** (the same as plot of *tert*-butylbenzene **10**) becomes atypical one (Fig. 3).

3.3.3. Effect of basic *ortho*-parameters *N-B-o* ($d_o^{H,N}$) on the ideal form of “real” plot

As it was mentioned above, the greatest difference between “real” and “ideal” plots is observed for their left branches. Let us pay attention to the cases when absolute values |Δ*N*-(*o*-*m*)| (given in Table 3 for 22 monosubstituted benzenes **1-13** and **18-26**) will exceed 100 mlrd. There are plots of compounds **6**, **10-11**, **13**, **18-20**, **22-23**, **25** and **26.** For each of these compounds the parameter Δ*N*-(*o*-*m*) has a positive sign and value from +150 to +500 mlrd.

When analyzing the parameters Δ*N*-(*o*-*m*) one can see that the main difference between the left branch of "real" and "ideal" plots is casued first of all by the shift of "real" absorbance of *ortho*-protons toward a low field. The shifts of *meta*-proton absorption play the minor role. Therefore we may assume that just differential parameter Δ*N*-*B*-*o* contributes to the difference between "real" and "ideal" plots. The parameter is equal to the difference between "real" and "virtual proportional" values of *ortho*-protons chemical shift.

3.3.4. Hypothesis about the influence of substituent *Y* voluminosity on the parameters Δ***N*-*B*-*o*** and Δ***N*-*B*-*m***

The compounds **1**, **6**, **10-11**, **13**, **18-20**, **22-23**, **25** and **26** have the largest positive values of parameter Δ*N*-*B*-*o* (from +120 to +500 mlrd., Table 2). This list (excluding compound **1,** we'll discuss it below) coincides with the list of compounds (Subsection 3.3.3.), the differential parameter of which is equal or exceeds +150 mlrd.

The low-field shifts of *ortho*-proton signals for 12 mentioned compounds are caused by the increase of substituent *Y* voluminosity[4] in them. Below we discuss in details all voluminous substituents *Y*.

To our mind this value has the greatest influence on the nearest *ortho*-protons. We assume that the effect occurs through the space. Probably we may neglect this influence on the most distant *para*-protons. It has some influence on *meta*-protons. The absolute values of difference parameters Δ*N*-*B*-*m* for the compounds **1, 4, 5, 11** and **25** within the range from +60 to +110 mlrd. (see above) indicate this fact. The highest value has the parameter Δ**1**-*B*-*m* = +110 mlrd. for *meta*-protons in aniline **1**. It is almost equal to the value of the similar *ortho*-parameter Δ**1**-*B*-*o* = +120 mlrd. Therefore these values offset each other in the difference parameter Δ**1**-(*o*-*m*) = Δ**1**-*B*-*o* – Δ**1**-*B*-*m* = +120 – (+110) = = +10 mlrd. As a result, the parameter does not get into the list of parameters Δ*N*-(*o*-*m*) exceeding 100 mlrd. It is the only one difference between the lists of monosubstituted benzenes with voluminous substitutents *Y* formulated in accordance with various differential parameters |Δ*N*-(*o*-*m*)| and Δ*N*-*B*-*o*, correspondingly.

3.4. Connection between Structural Peculiarities of Polyatomic Substituents and Values of ***Ortho***-Protons Chemical Shifts

In 21 of 26 monosubstituted benzenes (**1-11, 13, 18-26**) there are more than one atom in the substituent *Y*, *i.e.* such substituent is a polyatomic one. The atom connected with a phenyl ring is the "central atom". It is the element of the second period (C, N or O) or that of the third period (Si or S) in the examined polyatomic substituents *Y*.

3.4.1. The notion "branching" and "unsaturation" of polyatomic substituents

If the substituent *Y* contains only one fragment connected with the "central atom" and which is not hydrogen atom, we consider such substituent as a "non-branched" one. The example is the ethyl group in ethylbenzene **8**. If the "central atom" is bivalent oxygen or sulfur atom (compounds **3-6**) such substituents cannot be branched.

The majority of polyatomic substituents *Y* are the branched ones. Usually the center of branching is just "central atom", the valency of which is higher than 2. The substituents, where more than two fragments which are not hydrogen atoms (or fluorine atoms in trifluoromethyl substituent *Y* for the compound **21**) are connected with the "central atom", we call the branched substituents *Y.* In some cases the "central atom" of the substituent is connected with one of the fragments by a multiple (double) bond. We examine such substituents as unsaturated ones. The unsaturated substituent is considered to be branched even if its second fragment is hydrogen atom connected with the "central atom" (*e.g.* for benzaldehyde **23**). In such a case the double bond with one fragment is equated to two single bonds with two fragments.

The most considerable low-field shifts of *ortho*-protons were found for the compounds with branched polyatomic substituents *Y*, especially if they are unsaturated ones. Let us first examine the substituents the "central atoms" of which are elements of the second period (unsaturated and saturated) and then the substituents with the elements of the third period as the "central atoms".

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[4] Under voluminosity we mean more complicated notion than a simple physical volume of the substituent *Y*, because for example, the volume of long-chain analog of ethyl fragment – *n*-decyl ($–C_{10}H_{21}$) will be larger than that of branched *tert*-butyl fragment $–C(CH_3)_3$. The ratio between their "voluminosities" will be opposite.The effect of the substituent structure on its voluminosity is discussed below.

3.4.2. Unsaturated polyatomic branched substituents

The maximal parameters Δ*N-B-o* were found for the branched unsaturated polyatomic substituents *Y* the "central atoms" of which are elements of the second period. The greatest parameters are for benzoic acid **18** and its ethers **19** and **20** (substituent *Y* = –C(O)–OR, carbon is the "central atom"). They are equal to +480––490 mlrd. In nitrobenzene **26** (substituent *Y* = $-NO_2$, nitrogen is the "central atom") the value of the parameter Δ**26**-*B-o* is lesser and equals to +450 mlrd. It should be noted that for both types of substituent the "central atom" (C or N) is connected with the oxygen atoms of two fragments. One of them has a double bond (C=O or N=O) and the second one – the single bond (C-O or N-O).

In acetophenone **22** (substituent *Y* = $-C(O)-CH_3$) the "central atom" is connected with oxygen atom by the double bond and forms the carbonyl group. The second fragment (methyl group) is connected by the single bond, *i.e.* C–C bond, as for the compounds **18-20** the bond C–O is the single bond (or N–O in **26**). Probably it is the reason for smaller value of the parameter Δ**22**-*B-o* = +370 mlrd. The aldehyde group in benzaldehyde **23** is less voluminous than the acetyl group in **22** because hydrogen atom is connected to the central carbon atom as the second fragment, *i.e.* C–H instead of C–O in **18-20** or C–C in **22**. Probably the parameter Δ**23**-*B-o* = +210 mlrd. decreases due to the connection of the "central atom" with the least voluminous hydrogen atom by the single bond.

In diphenyl **11** (substituent *Y* = $-C_6H_5$) the carbon atom is the central one connected with two fragments by the double and single bonds C=C and C–C. The value Δ**11**-*B-o* = +260 mlrd. is smaller compared with above-mentioned "carbonyl" compounds with the double bond C=O.

Hence, the exchange of oxygen atom for the carbon atom (and especially for the hydrogen atom) in the fragment of the substituent *Y* connected with the "central atom" by both double and single bonds, decreases the parameter Δ*N-B-o*.

3.4.3. Polyatomic branched saturated substituents

For the compounds **1, 9** and **10** with branched but saturated substituents *Y* ($N(CH_3)_2$, $C(CH_3)_3$, $CH(CH_3)_2$) the parameter Δ*N-B-o* value is within the range from +100 to +250 mlrd. With decreasing the degree of alkyl group branching in the row *tert*-butylbenzene **10** (*Y* = $C(CH_3)_3$) → cumene **9** (*Y* = $CH(CH_3)_2$) → ethylbenzene **8** (*Y* = CH_2CH_3) → toluene **7** (*Y* = CH_3) the value of parameter Δ*N-B-o* sequentially decreases: 260 → 100 → 60 → 40 mlrd.

Let us note the closeness of the parameters Δ*N-B-o* for dimethylsubstituted compounds: dimethylaniline **1** (*Y* = $N(CH_3)_2$, Δ**1**-*B-o* = +120 mlrd.) and cumene **9** (*Y* = $CH(CH_3)_2$, Δ**9**-*B-o* = +100 mlrd.).

3.4.4. Polyatomic substituents with the "central atom" – element from the third period (S or Si)

For the compounds **6, 13** and **25** with the corresponding substituents $-SCH_3$, $-Si(CH_3)_3$ or $-SO_2CH_3$ we also observe the insignificant low-field shift of *ortho*-protons absorption: *Y* = $-SCH_3$ (Δ**6**-*B-o* = = +180 mlrd.); *Y* = $-Si(CH_3)_3$ (Δ**13**-*B-o* = +190 mlrd.) and *Y* = $-SO_2CH_3$ (Δ**25**-*B-o* = +230 mlrd.). Let us note that the parameter **25**-*B-o* = +230 mlrd. of the only one compound with unsaturated substituent (*Y* = $-SO_2CH_3$, the "central atom" is the element of the third period) is considerably less than the averaged value (≈ +400 mlrd.) for six compounds **18-20, 22-23** and **26** with unsaturated substituent and the "central atom" – element of the second period. At the same time for the compounds with saturated substituents and the "central atom" as the element of the third period (**6** and **13**) the parameters Δ*N-B-o* (+180 and +190 mlrd., respectively) are almost equal to the averaged value (≈ +160 mlrd.) of the compounds **1, 9** and **10** with the "central atom" – element of the second period.

3.4.5. Polyatomic non-branched saturated substituents

The compounds **2, 3-5, 7-8, 21** and **24** contain polyatomic substituents *Y* which we consider as non-branched near the "central atom". As a rule they have small positive values of the parameter Δ*N-B-o* (≤ 50 mlrd.); only parameter Δ**3**-*B-o* has the negative value. Let us pay attention to benzonitrile **24** with unsaturated substituent – nitrile group with triple bond –C≡N. To our mind, just linearity of this group, *i.e.* absence of branching near the carbon "central atom" is the reason for the absence of low-field shift of *ortho*-protons absorption.

Thus, the main factor that causes the low-field shift of *ortho*-protons absorption is branching of polyatomic substituent *Y*, *i.e.* the existence of branching near the "central atom" connecting the substituent and the phenyl ring. The existence of unsaturated bonds of the "central atom" (*e.g.* double bond C=O in the acetyl group in acetophenone **22** compared with the single bond C–C in ethylbenzene) considerably intensifies this low-field shift.

3.5. Connection between the Substituent *Y* Voluminosity and Brown *Para*-Constants

Let us consider the discussed earlier [7] change of coefficients of linear correlation *k* as the substantiation of assumption about the influence of voluminosity on the nearby protons (mainly *ortho*-protons). We discuss the dependence $\Delta d_o^{H,N} - s^+_p$ (or *N-D-o* – s^+_p), *i.e.* the dependence of *ortho*-protons chemical shift on the values of Brown *para*-constants in the monosubstituted benzenes **1-13** and **18-26** (excluding haloidbenzenes **14-17** and benzoic acid **18** [3]).

In the “combined” set discussed in [2] the values of Brown *para*-constants are given only for 17 from 21 monosubstituted benzenes (they are absent for the compounds **5, 22, 23** and **25**). If we do not divide the substituents *Y* by their voluminosity, then the coefficient *k* for all 17 monosubstituted benzenes is equal to 0.924 (Fig. 8 [7]).

In our previous work [7] we instinctively and arbitrarily divided 17 substituents *Y* into two types according to their voluminosity: i) voluminous substituents and ii) less voluminous substituents. In Fig. 9 the points of the same 17 monosubstituted benzenes are included into two plots. Eight points of the compounds with voluminous substituents compose the first plot and are denoted by squares; 9 points of the compounds with less voluminous substituents compose the second plot and are denoted by triangles.

For both plots we observe the increase of *k* coefficient: for the first plot it is 0.986 and for the second – 0.998 [7].

We arbitrarily chose 8 compounds (**1, 6, 10, 11, 13, 19, 20** and **26**) for the group with voluminous substituents. Almost all substituents in this group are branched (excluding thioanizole **6** with the “central atom” – element of the third period). Moreover the values of Δ*N-B-o* parameter for all mentioned compounds exceed +110 mlrd.

The group of 9 compounds (**2-5, 7-9, 21** and **24**) with less voluminous substituents coincides with the above-mentioned compounds **2-5, 7, 8, 12, 21** and **24**, which absolute values of Δ*N-B-o* do not exceed 60 mlrd. The only one exclusion is cumene **9**. Its substituent is isopropyl group $-CH(CH_3)_2$ which belongs to the group with branched polyatomic saturated substituents and its parameter Δ**9**-*B-o* = 100 mlrd. At the same time we have marked the point of cumene **9** as triangle, because it is situated closer to the line of the of the lower plot. Square points of *tert*-bitylbenzene **10** and trimethylphenylsilane **13** (two from three compounds with branched polyatomic saturated substituents) are situated below the line of upper plot and, correspondingly, closer to the line of lower plot.

So, polyatomic saturated branched substituents *Y* have the tendency to approach the line of the compounds with less voluminous substituents. The least branched isopropyl substituent in cumene **9** altogether transits to the group of compounds with less voluminous substituents.

Thus, it seems to be a fact that there is a quantitative connection between the deviation from linearity of the dependence $\Delta d_o^{H,N} - s^+_p$ and the effect of substituents voluminosity expressed by the values Δ*N-B-o*. The obtained results confirm the accuracy of assumption about the influence of voluminous substituents on the nearby *ortho*-protons through the space. As a result, the linear dependence between their chemical shift and experimental Brown constants is distorted.

If it is possible to account the spatial influence of voluminosity of the chemical shift, then the dependence of *ortho*- and *para*-protons absorption on electron parameters of the substituent *Y* will have the linear character. The electron parameters show the capability of substituent *Y* to conjugate with phenyl ring in monoalkylbenzenes **1-26** and quantitatively the values of Brown *para*-constants set take into account this ability in the best way.

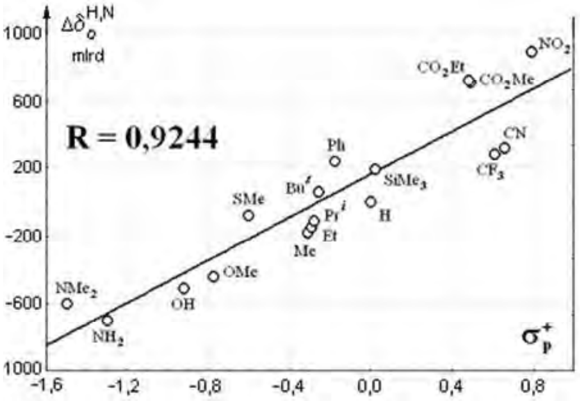

Fig. 8. Single-line dependence *N-D-o* – $s^+_p(\Delta d_o^{H,N} - s^+)$

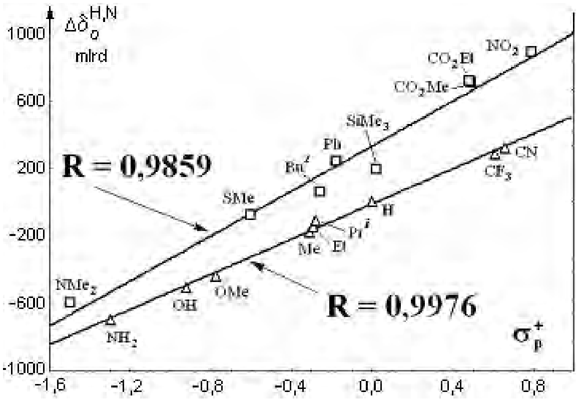

Fig. 9. Dual line dependence *N-D-o* – $s^+_p(\Delta d_o^{H,N} - s^+)$

4. Conclusions

1. The graphic example of ^{1}H NMR spectral parameters of three phenyl protons in monosubstituted benzenes has been developed.

2. It was shown that plots of proptons of all monosubstituted benzenes with electron-donor substituents are situated below the "benzene line" and have the "hill" form. The plots of the compounds protons with electron-acceptor substituents are above the "benzene line" and have the "pit" form.

3. We introduced the concept of virtual values of proton spectral parameters and proposed the method of their calculations and graphic images. The "virtual" and "real" plots of proton spectral parameters were compared for the most of investigated monosubstituted benzenes.

4. The deviation of "virtual" plots from the "real" ones is caused by the increase of substituent *Y* "voluminosity". The effect of substituent structure on its voluminosity was examined.

5. The substituents *Y* were divided into two types depending on semi-quantitative estimation of their "voluminosity". The dependence of *ortho*-protons chemical shift from Brown "*para*-constant" (dual-line plot) was plotted for every type of the substituents. Very high values of linear correlation coefficients (0.986 and 0.998) were obtained for two plots. These coefficients are closer to the one compared with that of the similar plot (0.924) drawn for all monosubstituted benzenes without taking into account the substituent "voluminosity" (single-line plot).

6. In the dual-line plot the high correlation coefficients of *ortho*-protons chemical shift depending on Brown *para*-constants allow to admit the presence of linear dependence between values of chemical shift not only for *para*-protons but for *ortho*-protons as well.

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ВПЛИВ ГЕОМЕТРИЧНИХ ПАРАМЕТРІВ ЗАМІСНИКА НА ВЕЛИЧИНИ ХІМІЧНИХ ЗСУВІВ ОРТО- І МЕТА-ПРОТОНІВ В ЯМР ^{1}Н СПЕКТРАХ МОНОЗАМІЩЕНИХ БЕНЗОЛІВ

Анотація. *Наведено спектральні (ЯМР ^{1}Н) параметри протонів фенільного кільця в 26 монозаміщених бензолах C_6H_5-Y (включаючи сам бензол). В аналітичному і графічному вигляді проаналізовано величини хімічних зсувів орто-, мета- і пара-протонів, а також різниці між величинами їх поглинання. Введено концепцію ідеальних графіків для трьох типів фенільних протонів. Розглянуто поняття «об'ємності» замісника, її залежність від хімічної структури замісника і вплив на величину поглинання орто-протонів. Показано, що з врахуванням «об'ємності» замісника можна побудувати графіки залежностей хімічного зсуву орто-протонів від констант Брауна з дуже високим (99 % і вище) коефіцієнтом кореляції.*

Ключові слова: *ЯМР ^{1}Н спектр, монозаміщені бензоли, хімічний зсув, протон, константа Брауна.*