

DEPENDENCE OF SPECTRAL PARAMETERS IN ¹H AND ¹³C NMR SPECTRA OF AROMATIC COMPOUNDS UPON SUBSTITUENT SPATIAL-STRUCTURAL PECULIARITIES

1. Main regularities of the effect of alkyl groups spatial structures on the chemical shift of aromatic *ortho*-protons in monoalkylbenzenes NMR ¹H spectra

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Abstract

The presence of opposite by δ_o^H shifts of *ortho*-protons (downfield, if the substitution takes place in α -position and upper-field – in β -position) by the substitution of hydrogen atoms for methyl groups in alkyl chain of alkylbenzenes has been found. The independent influence of both effects at the simultaneous branching near α - and β -hydrocarbon atoms of alkyl chain has been determined. The mentioned phenomena has been explained by conformational peculiarities of alkylbenzenes structure.

Key words: alkylbenzenes, chemical shift, Hammett constant.

Introduction

While studying the interrelation between δ_{ar}^H chemical shifts of phenyl protons in the ¹H NMR spectra of mono-substituted benzenes and constants (σ_p and σ_p^+) of the substituent group it has been shown [1, 2] that δ_p^H value has good correlation with Okamoto-Braun constant (σ_p^+) (correlation coefficient $R \sim 0.96-0.97$) and worse one with Hammett constant (σ_p) for the protons in *para*-position regarding substituent group.

Since in mono-substituted benzenes orienting effect of substituent is the same by sign for *ortho*- and *para*-positions and opposite for *meta*-position, it was interesting to find the possible connection between constants of substituent and chemical shifts of protons in the *ortho*-position, i.e. δ_o^H parameters. Universally recognized constants, analogous to σ_p and σ_p^+ constants, are absent

for *ortho*-positions of phenyl nuclear and application of constants for *para*-substituent is not well-posed. However, such correlation exists but it is essentially worse ($R \sim 0.9$) than that for *para*-protons.

As a rule, steric factor is the reason of correlation worsening of *ortho*-protons, spatially approximated to the substituent. At the same time we may neglect their contribution to the σ_p and σ_p^+ constants of the phenyl ring.

In order to determine the peculiar effect of substituent spatial factors on δ_o^H parameters the alkyl groups are the best types of substituent. Alkyl substituents may differ by steric parameters but all of them have similar polar properties. Moreover, their characterizing constants σ_p and σ_p^+ are located in a narrow interval [3]. The main contribution into the difference between chemical shifts of *ortho*-protons (δ_o^H) and *para*-protons (δ_p^H) of monoalkylbenzenes should be done by spatial constituents. The slight difference between electronic factors for different alkyl substituents may be neglected.

It is advisable to divide all alkyl groups by two kinds: linear and branched. Whereas linear alkyl groups are similar between each other by steric parameters and differ only by chain length, branched alkyl groups may have essential differences in their structures. The main characteristic factors for branched alkyl groups are: i) the position of branch point in a chain; ii) number of branches in this point; iii) number of branch points in the main chain of alkyl group. The spatial approach of the chain fragment takes place at the branching of alkyl substituents in comparison with linear groups. This phenomenon may change the value of δ_o^H parameter. Using known literature 1H NMR spectra of monoalkylbenzenes we investigated the effect of above-mentioned factors on the values of δ_o^H parameter.

For branched monoalkylbenzenes it is advisably to study effects of both factors on the δ_o^H parameter: number of branches in one point and position of this point in the alkyl chain. To achieve this aim all molecules were divided into two parts: nonvarying fragment for all molecules and fragments varying from molecule to molecule. Three variable fragments R^1 , R^2 , R^3 (by valence number of connected hydrocarbon atom) are hydrogen atom or methyl group and designated by italics. Four types of $-CR^1R^2R^3$ alkyl group with different R are in the raw with nonvarying fragment: 1) methyl group ($R^1 = R^2 = R^3 = H$); 2) ethyl group ($R^1 = R^2 = H$, $R^3 = Me$); 3) isopropyl group ($R^1 = H$, $R^2 = R^3 = Me$) and 4) *tert*-butyl group ($R^1 = R^2 = R^3 = Me$). At the first stage we investigated the effect of branching increase near the nearest to the phenyl ring α -hydrocarbon atom of alkyl chain and at the second and third stages – near β - and γ -hydrocarbon atoms.

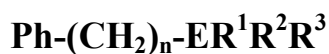
Toluene **IIa**, ethylbenzene **IIb**, cumene **IIc** and *tert*-butylbenzene **IId** are in the series of alkylaromatic compounds with the branching at α -position of the side chain by general formula $Ph-CR^1R^2R^3$ **II**. On the transition from **IIa** to **IId**

there is a consecutive and uniform volume increase of alkyl substituent near the studied *ortho*-aromatic hydrogen atoms (H-2 and H-6). Ethylbenzene **IIIa**, propylbenzene **IIIb**, isobutylbenzene **IIIc** and neopentylbenzene **IIId** are in the series of alkylaromatic compounds with the branching at β -position of the side chain by general formula $\text{Ph-CH}_2\text{-CR}^1\text{R}^2\text{R}^3$ **III**. Propylbenzene **IVa**, butylbenzene **IVb**, isoamylbenzene **IVc** and 3,3-dimethylphenylbenzene **IVd** are in the series of alkylaromatic compounds with the branching at γ -position of the side chain by general formula $\text{Ph-CH}_2\text{-CH}_2\text{-CR}^1\text{R}^2\text{R}^3$ **IV**. A consecutive and uniform volume increase of alkyl substituent of the components from the series **III** and **IV** takes place at the some distance of hydrogen atoms H-2 and H-6.

In order to study the effect of branch point number on the δ_o^{H} parameter we have chosen the series by general formula $\text{Ph-CR}^1\text{R}^2\text{-CH}_2\text{CH}_3$ **V**. Such series are the only ones for which data of ^1H NMR spectra are reliable. Two variable fragments R^1 and R^2 near α -hydrocarbon atom are hydrogen atom or methyl group and R^3 fragment is ethyl group in all cases. The latter may be considered as a group with additional branch point (near β -hydrocarbon atom of the general alkyl chain). Moreover, this point has only one branching, i.e. there are two hydrogen atoms and one methyl group.

Due to the near resemblance of alkyl substituents in the series **I-V** some alkylbenzenes may be simultaneously in two or more series. Thus, ethylbenzene **IIb** is in the series **II**, as well as in the series **III**. In the series **III** it should have the number **IIIa** and propylbenzene **IIIb** – in the series **IV** and **V** (**IVa** and **Va** correspondingly).

For the comparison of two series of phenyl-containing silanes: phenylalkylsilanes **VI** and benzylalkylsilanes **VII** we have also used ^1H NMR spectra. These series differ from the series **II** and **III** by the substitution of hydrocarbon atom for the silicon one in the branch point: at α -position in the series **VI** and β -position in the compound **VIIId**. The definite analogy with the series of α -branched alkylbenzenes **II** exists for the series of branched alkanes **VIII**.



I-IV, VI, VII



V



VIII

here: E = C (**I-IV**), Si (**VI, VII**); n = 3-16 (**I**), n = 0 (**II**), n = 1 (**III**), n = 2 (**IV**); $\text{R}^1, \text{R}^2, \text{R}^3 = \text{H}$, Me: **a)** $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{H}$; **b)** $\text{R}^1 = \text{R}^2 = \text{H}$, $\text{R}^3 = \text{Me}$; **c)** $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{R}^3 = \text{Me}$; **d)** $\text{R}^1 = \text{R}^2 = \text{R}^3 = \text{Me}$.

Experimental

We have used only literature values of δ_o^H chemical shift for compounds **I–VIII** obtained from 1H NMR spectra in deuteriochloroform. To minimize the inaccuracies connecting with the difference between δ_o^H values for the same compound¹, it is desirable to take all δ_o^H values from one source of information because all data from the one source coordinate with each other. However we had to take data from two sources: atlas of NMR spectra by “Aldrich” [5] and internet-site [6]. They are the most reliable because each of them contain spectra which are absent in the other one.

We have determined the doublet signals centers of *ortho*-protons in the spectra from [5] with the accuracy of 0.005 ppm. The accuracy of all spectra in [6] is usually 0.001 ppm. Values δ_o^H presented in the both sources differ by no more than 0.02 ppm. In some cases the difference was larger². Therefore, we decided to “unite” data from both sources and inaccuracy of measurements was ≤ 0.02 ppm. If δ_o^H values from [5] did not coincide with those from [6], we used data from [5]. All used for the calculation δ_o^H values are rounded off to 0.01 ppm and underlined.

Values δ_o^H are practically the same and equal to 7.16–7.18 ppm [5, 6] in all linear alkylbenzenes **Ia** with C_4H_9 – $C_{20}H_{41}$ alkyl groups. For alkylbenzenes **II–VII** in [5] and [6] δ_o^H values are in Table:

Compounds	δ_o^H , ppm in [5]	δ_o^H , ppm in [6]
IIa	7.14	-
IIb	7.18	-
IIc	7.21	7.231
II d	7.385	-
IIIb	7.16	-
IIIc	-	7.14
III d	7.11	-
IVb	7.16	7.18
IVc	7.18	-
IV d	-	-

¹ Difficulties during comparison of the same basic spectral parameters δ^H obtained from different literature data were discussed in [4].

² Maximum difference of 0.07 ppm between δ_o^H values was recorded for Ph_3SiMe . The comparison of other δ^H spectral parameters allows to assume that there is a shift (is not depicted in the spectrum) of standard compound signal to the upper field approximately by 0.07 ppm in the spectrum given in [6]. Therefore, all other signals also are shifted to the upper field by 0.07 ppm. To our mind, the correct data are in [5].

Vb	7.17	-
Vc	-	7.31
VIa	7.58	-
VIb	-	-
VIc	7.54	7.527
VIId	7.515	7.447 ²
VIIId	6.995	6.985

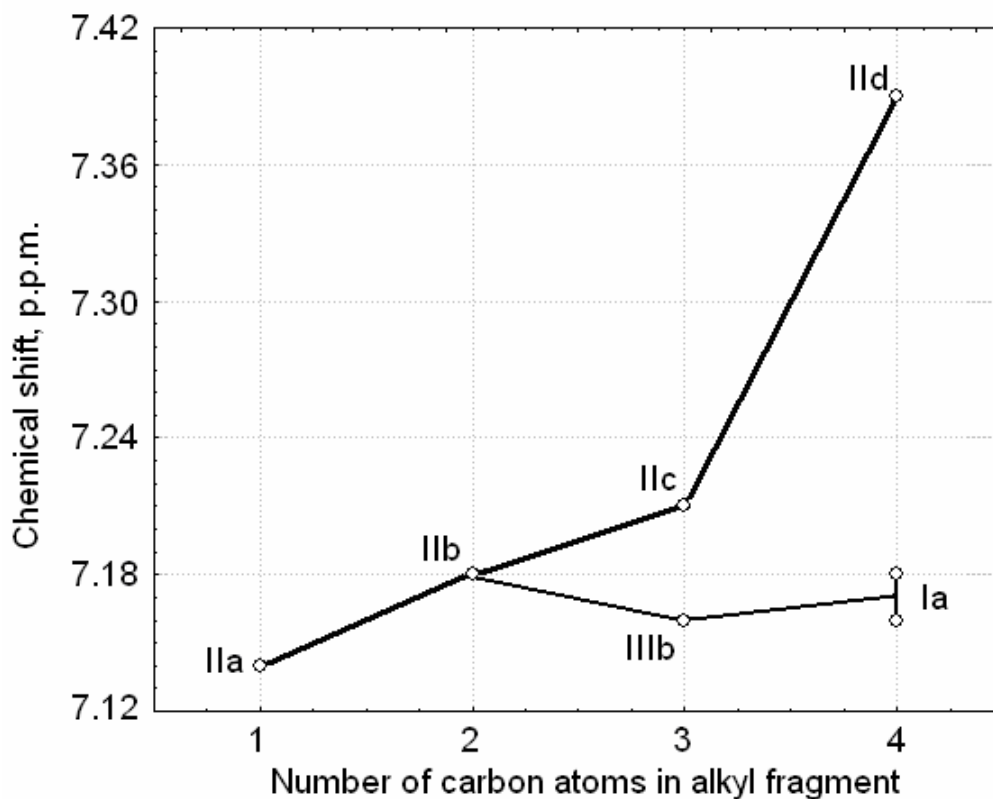
For the underlined hydrogen atom in the series **VIII** values δ^H are following [6]: 1.39 ppm in **VIIIa**, 1.56 ppm in **VIIIb**, 1.639 ppm in **VIIIc** and 1.974 ppm in **VIIId**.

Results and Discussion

Analyzing the spectral parameters of alkylbenzenes united in the series **I–IV**, we have found the simple dependences of δ_o^H values upon spatial factors stipulated by alkyl group structure. In **Figs. 1** and **2** values δ_o^H are connected with straight lines as far as a number of methyl groups in R^1 , R^2 , R^3 fragments increases. As a result, each series **I–IV** have broken lines consisting of three straight sections (branches). Following regularities were received.

One can see from **Fig. 1** that the length of alkyl chain in the linear long-chain (C_4 – C_{20}) alkylbenzenes **Ia** does not affect the chemical shift of *ortho*-protons. Compounds with shorter alkyl chains (CH_3 , C_2H_5 and n - C_3H_7) are examined in other series.

Fig.1. Change of δ_o^H parameters in the rows: a) **IIa** \rightarrow **IIb** \rightarrow **IIIa** \rightarrow **Ia** (fine line); b) **IIa** \rightarrow **IIb** \rightarrow **IIc** \rightarrow **IId** (heavy line).

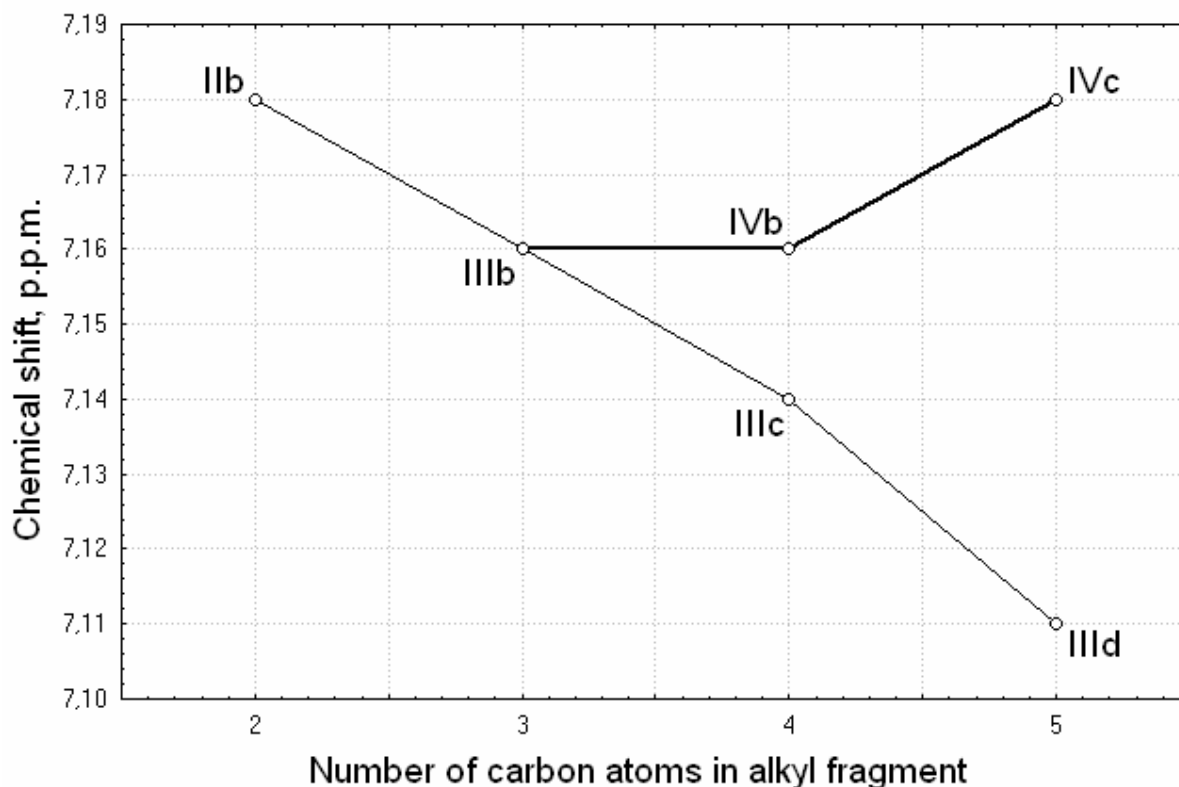


Substitution of hydrogen atoms for methyl groups in the series of α -branched alkylbenzenes **IIa** \rightarrow **IIb** \rightarrow **IIc** \rightarrow **IId** leads to a monotonic shift to downfield of aromatic *ortho*-protons H-2 and H-6. This shift is small (~ 0.03 – 0.04 ppm) at the transition from toluene to ethylbenzene and further to cumene, but increases sharply (to ~ 0.18 ppm) at the transition from cumene to *tert*-butylbenzene.

Substitution of hydrogen atoms for methyl groups in the series of β -branched alkylbenzenes **IIIb** \rightarrow **IIIb** \rightarrow **IIIc** \rightarrow **IIId** leads to a monotonic shift to upper field of δ_o^H parameter. This small shift is practically constant for every step and equal to ~ 0.02 – 0.03 ppm.

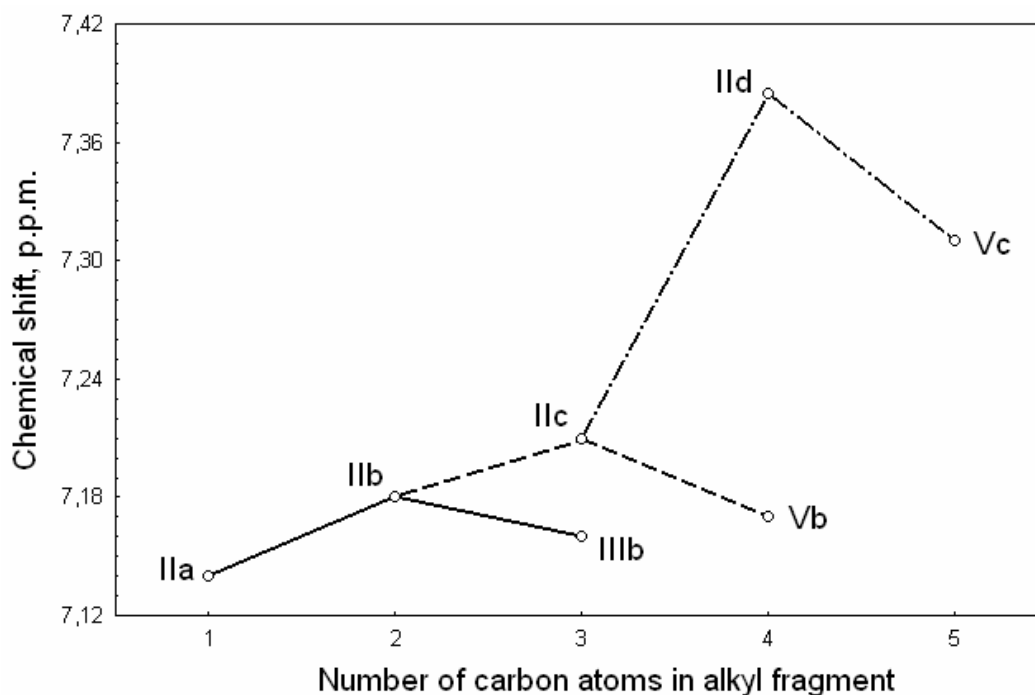
The change of δ_o^H parameter in the incomplete series **IV** is small and stayed in the limits of experimental error.

Fig. 2. Change of δ_o^H parameters in the rows: a) **IIb** \rightarrow **IIIb** \rightarrow **IIIc** \rightarrow **IIId** (fine line); b) **IIIb** \rightarrow **IVb** \rightarrow **IVc** (heavy line).



In more complicated cases in series **V** substitution of two hydrogen atoms for two methyl groups first at α -, and then at β -position leads to the simultaneous influence of aromatic ortho-protons on the chemical shifts but in opposite directions. We assume that α - and β -effects in the series **V** are independent. In **Fig. 3** there are three series of “triad” – broken lines consisting of two branches and representing the transition from initial compound **IIa**, **IIb** or **IIc** to α -, β -dimethyl substituted compound **V** (**IIIb**, **Vb** and **Vc**, correspondingly) through α -methyl substituted derivative (**IIb**, **IIc** correspondingly). Every broken line has “hill” form with ascending left branch (α -substitution) and descending right branch (β -substitution). The triad **IIa** \rightarrow **IIb** \rightarrow **IIIb** is designated by firm line, **IIb** \rightarrow **IIc** \rightarrow **Vb** is designated by dotted line and **IIc** \rightarrow **IIId** \rightarrow **Vc** – dash-dot line. Let us mark the steepest increase and decrease of *tert*-butyl derivative triads **IIc** \rightarrow **IIId** \rightarrow **Vc**.

Fig. 3. Change of δ_o^H parameters in the monoalkylbenzene “triads”.



We explain peculiarities of δ_o^H parameters of alkylbenzenes in the series **IIa–IIId** by the following.

Let us examine differential parameters $\Delta\delta_o^N = \delta_o^N - \delta_o^M$ of the four alkyl substituents. Symbol “M” means the methyl group, where only hydrogen atoms are variables. Symbol “N” means other groups Et, Prⁱ, Bu^t where methyl group is one (or more) variable fragment. Differential parameters $\Delta\delta_o^{Et} = 0.04$ ppm (for *ortho*-ethyl) and $\Delta\delta_o^{Pr} = 0.07$ ppm (for *ortho*-isopropyl) are smaller by an order than $\Delta\delta_o^{Bu} = 0.25$ ppm parameter (for *ortho*-*tert*-butyl substituent).

If C-7 atom is situated in the tetrahedron center and C-1 atom – in its vertex, then three variable parameters R^1, R^2, R^3 are situated in three angles of the base. It is reckoned that in alkylbenzene molecules alkyl substituent rotation takes place around C-1–C-7 bond, i.e. rotation of tetrahedron base around perpendicular axis. Different spatial arrangements of R^1, R^2, R^3 fragments relative to the plane of Ph-C static fragment, i.e. molecule different conformations, may be fixed while rotation.

Let us see the **IIb** or **IIc** alkylbenzene rotation, because R^2 structure has no mean in this case. We can see on **Fig. 4** the conformation where R^1 fragment is in the plane of Ph-C static fragment and therefore it comes close to H-2 atom most of all. Two fragments R^2 and R^3 are located, correspondingly, over and under the plain of benzene ring. There are five atoms (H-2, C-2, C-1, C-7 and central atom of variable fragment, i.e. hydrogen atom in this case) in the plain under study. At the rotational displacement counterclockwise by 120° B-

conformation is formed (**Fig. 5**). There are four static atoms of phenyl ring (H-2, C-2, C-1, C-7), as well as hydrocarbon atom of methyl group in it. It means that centre of R^3 variable fragment is in the plain and three hydrogen atoms are in the space outside the plain. R^1 and R^2 variable fragments are located over and under the plain of benzene ring.

Fig. 4. A-conformation for alkylbenzenes **IIb** and **IIc**

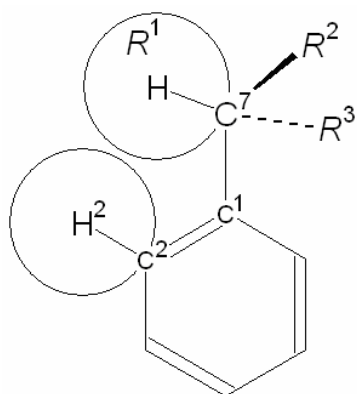
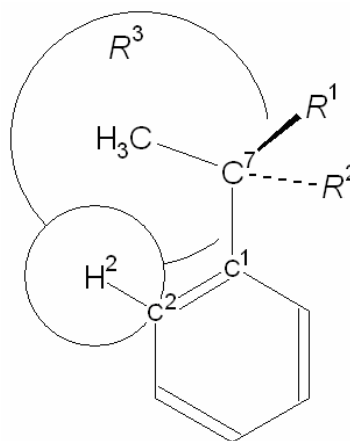


Fig. 5. B-conformation for alkylbenzenes **IIb** and **IIc**



Virtual molecule represented on **Figs. 4, 5** was formed using averaging lengths of C–C and C–H bonds, as well as angles between them. Effective Van der Waals spheres are designated by circles around maximum closed H-2 atom and R^1 (R^3) fragment. Data for the bond lengths and sphere radii are taken from [3].

One can see from **Fig. 4** that in A-conformation effective Van der Waals spheres of two hydrogen atoms H-2 and R^1 do not overlapped. Hence, we may assume only minor interference. In B-conformation there is a considerable overlap of H-2 hydrogen atom and R^3 methyl group resulting in essential interference, which is stronger than interference of two hydrogen atoms in A-conformation.

We assume that maximum closed to H-2 atom R^1 (R^3) fragment has the greatest influence on δ_o^H parameter. The influence of R^2 and R^3 (R^1) variable fragment is negligible. Hence, the main contribution into $\Delta\delta_o^N$ differential parameter will be determined by the effect of methyl group (variable R^3 fragment) in B-conformation in alkylbenzenes **IIb** and **IIc**, where both conformations are possible.

In alkylbenzenes **IIa**, **IIb** and **IIc** hydrogen atom is at least one of three variable fragments R^1 , R^2 and R^3 , whereas in **IId** all three fragments are methyl groups. Therefore three options of A-conformation and no options of B-

conformation are possible for toluene ($R^1 = R^2 = R^3 = H$). Two options of A-conformation and one B-conformation are possible for ethylbenzene ($R^1 = R^2 = H$, $R^3 = Me$); A-conformation and two options of B-conformation – in cumene. There are three options of B-conformation and no A-conformation in *tert*-butylbenzene.

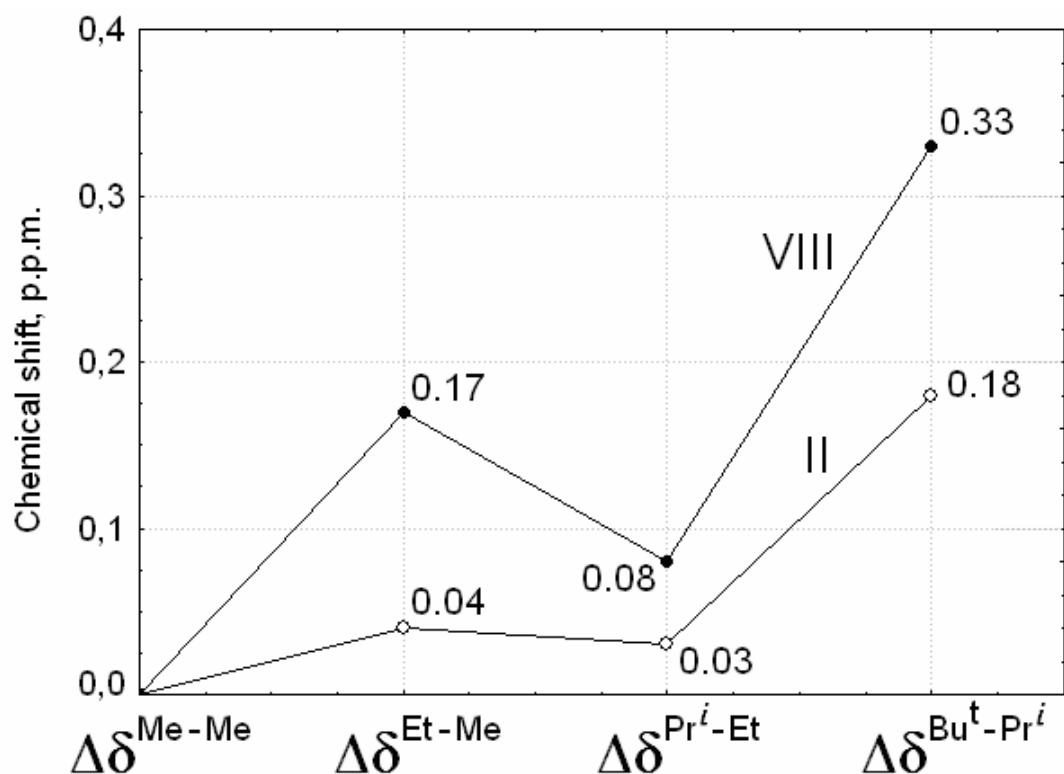
The methyl substituent in toluene might exist only in A-conformation. We assume that for ethyl and isopropyl substitutes A-conformation has the greater occupancy and less energy because of the less spatial difficulties and so A-conformation has greater role in the amount of all conformations. In other words, at the rotation of Et or Prⁱ alkyl substituent around C-1–C-7 bond the molecule stays longer in A-conformation than in B- (and may be other) conformations.

We may assume also that contribution of B-conformation in the amount of all conformations increases the effect of *ortho*-ethyl and *ortho*-isopropyl substituents on the downfield shift of δ_o^H parameter compared with *ortho*-methyl substituent though their values are comparable. Therefore $\Delta\delta_o^{Et}$ and $\Delta\delta_o^{Pr}$ characteristic differential parameters have small positive values.

The *tert*-butyl group exists by definition only in B-conformation and downfield shift of δ_o^N parameter must be maximum possible. Therefore $\Delta\delta_o^{Bu}$ differential parameter has positive value greater by an order of magnitude than $\Delta\delta_o^{Et}$ and $\Delta\delta_o^{Pr}$ parameters. That is why there is a great difference between $\Delta\delta_i^{Et}$, $\Delta\delta_i^{Pr}$ and $\Delta\delta_i^{Bu}$ values. The same explanations may be used for those conformations of alkylbenzene molecules **II** where no variable fragments (R^1 , R^2 and R^3) are located in the plain of phenyl ring.

Interesting results have been obtained at the comparison of δ_o^H parameters in the series of alkylbenzenes **IIa** → **IIb** → **IIc** → **IIId** with δ^H parameters in the similar series of branched alkanes **VIIIa** → **VIIIb** → **VIIIc** → **VIId**. Analogously to alkylbenzenes **II** the substitution of hydrogen atoms for methyl groups in the series **VIII** leads to the monotonic downfield shift of δ^H value, but here it is greater (0.17 → 0.08 → 0.33) against (0.04 → 0.03 → 0.18) in the series **II**. Symbasis of $\Delta\delta^N$ values is observed for both series with the increase of methyl groups amount in R^1 , R^2 , R^3 (**Fig. 6**). In both cases at the transition from methyl group to the ethyl one the growth of $\Delta\delta_o^N$ value is greater than that at the transition from ethyl to isopropyl group. The transition of isopropyl to *tert*-butyl group causes the more considerable jump of δ_o^N value in both cases.

Fig. 6. Dependence of ($\Delta\delta_o^N = \delta_o^N - \delta_o^M$) differential parameters for the series **II** and **VIII**.



Similarity of δ_o^N behavior in both cases we may explain by relative contents of hindered and screened conformations for **VIII** compounds. Probably the hindered conformation predominates for less sterically difficult compounds **VIIIa**, **VIIIb** and **VIIIc** (**Fig. 7**). Branched tert-butyl group in **VIII d** causes the rotation around C–C bond due to the repulsion from the nearest methyl group and reduces the dihedral angle till value close to 0° resulting in screened conformation (**Fig. 8**). Investigated hydrogen atom, both hydrocarbon atoms forming C–C bond and centre of *tert*-butyl group (quaternary hydrocarbon atom) are located in mentioned conformation in the same plain. Comparing **Figs. 5** and **8**, one can see that in both cases (compounds **IId** and **VIII d**) there is a similar arrangement of five hydrocarbon and hydrogen atoms. Therefore we can apply all arguments concerning B-conformation in **IId** compound for screened conformation in **VIII d** compound. It is possible explanation of similar effect of *tert*-butyl groups on the δ_o^H parameter in **IId** and δ^H parameter in **VIII d**.

There are also two options of conformation with substituent located in the plain of phenyl cycle in the series **IIIa-d** at the consecutive increase of methyl group number in R^1 , R^2 , R^3 variable fragments near β -hydrocarbon atom: A-conformation (**Fig. 4**, hydrogen atom is a substituent) and B-conformation (**Fig. 5**, $-\text{CH}_2\text{-CR}^1\text{R}^2\text{R}^3$ alkyl group is a substituent). Substitution of hydrogen atoms

in methyl group of ethylbenzene **IIb** for methyl groups at the transition **IIa** → **IIIb** → **IIIc** → **IIId** increases volume of $-\text{CH}_2-\text{CR}^1\text{R}^2\text{R}^3$ fragment and thereby increases role of A-conformation in these series. Moreover, $-\text{CH}_2-\text{CR}^1\text{R}^2\text{R}^3$ alkyl group is located in the space outside of phenyl ring plain. Therefore we assume that comparative role of A-conformation is enlarged causing the minimum shift of H-2 aromatic proton. The role of B-conformation is reduced. This conformation mainly contributes into downfield shift of *ortho*-proton signal in ^1H NMR spectra.

Fig. 7. Hindered conformation for **VIII**

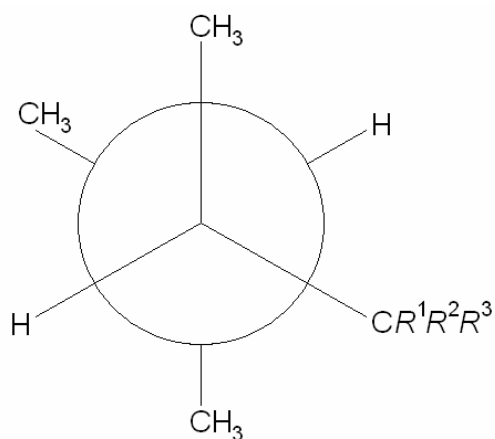
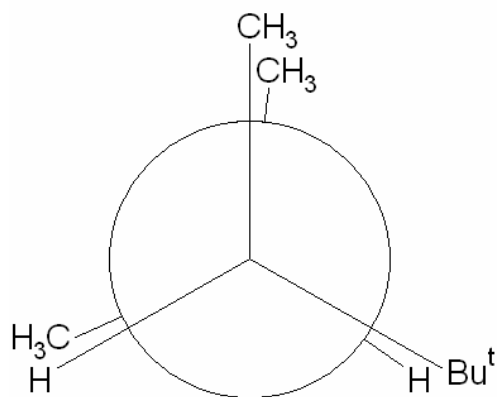


Fig. 8. Screened conformation for **IIId**.



We may assume that alkylbenzenes with alkyl groups of definite structure directly influence on *ortho*-position hydrogen atoms of phenyl ring through the space. Whereas branching near α -hydrogen atom shifts δ_0^{H} parameter toward downfield (positive values of $\Delta\delta_0^{\text{N}}$ differential parameters) and branching near γ -hydrogen atom practically does not influence it, viz. branching near β -hydrogen atom considerably shifts δ_0^{H} parameter to the upper field. Probably in the last case there is an optimum for upper-field shift of δ_0^{H} parameter accordance of geometrical ratio between two parts of the molecule: phenyl ring and $-\text{CH}_2-\text{CR}^1\text{R}^2\text{R}^3$ alkyl fragment. The larger volume of corresponding part of $-\text{CH}_2-\text{CR}^1\text{R}^2\text{R}^3$ (i.e. R^1 , R^2 , R^3 fragments), the larger upper-field shift of δ_0^{N} parameter (negative values of $\Delta\delta_0^{\text{N}}$ differential parameters).

In trimethylsilane **VIIId** there is a considerable upper-field shift of δ_0^{H} parameter compared with neopropylbenzene **IIIId** ($\Delta\delta_0^{\text{H}} = \delta_0^{\text{Si}} - \delta_0^{\text{C}} = 7.00 - 7.11 = 0.11$ ppm). The only difference in the structures of **IIIId** and **VIIId** compounds is nature of the atom in the branch point at β -position toward phenyl group. Substitution of hydrocarbon atom in **IIIId** for silicon atom in **VIIId** lengthens

both C–Si bonds (compared with C–C bonds) and changes C–Si–C angles. We assume that these changes increase the role of that conformation, which directly influences H-2 aryl hydrogen atom through the space and leads thus to the upper-field shift of δ_0^{H} parameter compared with δ_0^{H} parameter in **III**d.

The existence of direct influence through the space but not the transfer of effect by alkyl chain we may explain by following. If transfer of effect takes place by alkyl chain, we would see the more negative value of $\Delta\delta_0^{\text{H}}$ parameter due to the chain shortening in the analogous pair *tert*-butylbenzene **II**d–trimethylphenylsilane **VI**d (formed as a result of α -atom substitution for silicon atom in **II**d at preservation of the rest atoms). However, we see opposite ratio in the pair **II**d–**VI**d ($\Delta\delta_0^{\text{H}} = \delta_0^{\text{Si}} - \delta_0^{\text{C}} = 7.39 - 7.52 = +0.13$ ppm).

This difference, to our mind, may be explained as following: in the pair **II**d–**VI**d the chain length till the branch point is shorter than that in the pair **III**d–**VIII**d. Therefore, this length is insufficient for direct influence through the space on the H-2 atom. Moreover, configuration of groups connecting with β -atom is different because all three substituents are hydrogen atoms. Hence, the corresponding structure of substituent and β -position in the branched space relatively to the phenyl ring are the main factors for the spatial influence of alkyl group on δ_0^{H} parameter in alkylbenzenes of the series **III**.

Both mentioned reasons may explain the observed upper-field shift of δ_0^{H} parameter in the compounds **III**a–**III**d as a result of substitution of hydrogen atoms for methyl groups near β -hydrocarbon atom. Probably, branching near γ -hydrocarbon atom is very distant from C-2 and C-6 ortho-hydrogen atoms and therefore its influence on the shift of δ_0^{H} parameter is minimum.

Obtained regularities (as we'll show in the next articles) have been found in substituted alkylaromatic compounds including polyalkylbenzenes.

The comparison of dependence of δ_0^{H} parameters upon point branch number in two series of α -branched compounds – alkylbenzenes **II** and phenylsilanes **VI** – is of great interest. In spite of data absence for phenylmethylsilane **VI**b in [5] and [6]³, the general tendency in the series **VI** is clear: a considerable upper-field shift, which is typical for the series **III** of β -substituted alkylbenzenes, takes place instead of expected downfield shift of δ_0^{H} signals as for the series **II** of α -methyl substituted alkylbenzenes. This example warns us against mechanical transference of obtained regularities to the aromatic compounds similar by their structures.

³ The comparison of δ^{H} basic spectral parameters taken from [5] for the compounds of phenylsilane series $\text{PhSiH}_3 - \text{Ph}_2\text{SiH}_2 - \text{Ph}_3\text{SiH}$, as well as Ph_2SiMe_2 Ph_3SiMe allows to assume that δ_0^{H} values for the **VI**b compound should not considerably differ from other compounds in the series **VI**.

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