Volodymyr Mizyuk and Volodymyr Shibanov

INTERACTION BETWEEN MOLECULE FRAGMENTS UNBOUND BY CHEMICAL BONDS THROUGH THE SPACE DURING NMR ^{1}H SPECTRA REGISTRATION

Ukrainian Academy of Printing, Lviv, Ukraine, e-mail: vlm46@mail.ru

Abstract. The analysis of chemical shifts in NMR ^{1}H spectra of the *para*-substituted propylbenzens by general formula: *p*-X-C_6H_4-$CRR^1CH_2CH_3$ (where R, R^1= H, CH_3) was made. The presence or absence of the aryl fragment influence on the end methyl group was judged on the value of the basic spectral parameters - the chemical shifts of methyl protons ($\delta_{CH3}{}^{H}$) in comparison with analogous data of corresponding alkanes. There were developed and validated specific criteria for identifying such effect. We make the overall conclusion about high probability of the reciprocal intramolecular interactions between unbound fragments of molecule in *tert*-amylbenzene and *tert*-amylphenol **(**R = R^1 = CH_3).

Keywords: NMR ^{1}H spectra, *para*-substituted propylbenzens, basic spectral parameters, experimental differential parameters, virtual differential parameters, intramolecular interactions between unbound fragments of molecule.

1. Introduction

While analyzing the peculiarities of NMR ^{1}H and ^{13}C spectra of different classes of organic compounds we suppose that under recording spectra conditions the intramolecular interactions between unbound fragments of molecule may take place through the space. The existence of mentioned interactions leads, to our mind, to the observed changes in spectra compared with anticipated (expected) values.

The schematic drawing of investigated molecule containing fragments “K-L-M” is represented in Fig. 1. The arbitrary division into the fragments is in accordance with functional principle and depends upon the formulated aim. The aim is the investigation of NMR spectral parameters of the fragment “M” depending upon the structure of the fragment “K”. The absence of chemical bonds between atoms of the fragments “K” and “M” is an indispensable condition. Both fragments are bound by chemical bonds only with “medium” fragment “L”, with its opposite sides.

Fig.1

In the linear conformation **1** the interaction of unbound fragments “K” and “M” is absent. It is possible in the curved conformation **2**. To our mind, the deviation of spectral parameters of the fragment “M” from the anticipated values reveals about this.

The transition states with curved conformations, the same as **2**, are well-known in the synthetic chemistry, e.g. in the reactions of electrophylic cyclization or in substitution reactions proceeding with the transfer of reaction centre. Similar transition state was given in an article [1] describing NMR ^{17}O spectra of crowded alcohols, where authors had postulated through-space interaction in CH_3---O.

We suppose the following explanation of the observed phenomenon in accordance with the postulate: “*The possible interaction between two energy states* **occurs always** *under the given conditions if it* **leads to the decrease of the system total energy**”.

The changes of energy levels of two-component system taking place during their interaction are represented in Fig. 2. At the initial state “A” the interaction between energy levels of its components (A^1 and A^2) does not occur. The result is the system transition to its new state “B”. In this connection two new energy levels (B^1 and B^2) are formed and new system occupies a lower energy level (state B^1).

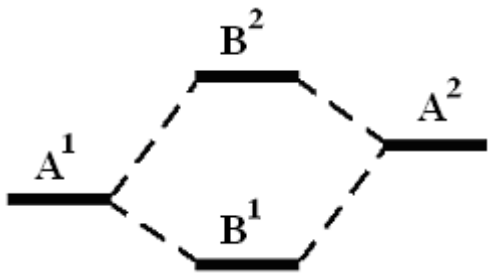
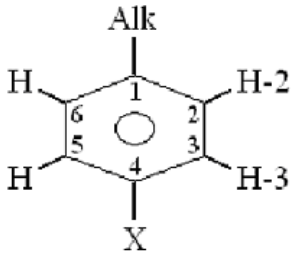


Fig. 2

It is logically to suppose that intramolecular interaction of unbound fragments of the molecule through the space in the conformation **2** leads to some energy gain (the decrease of the total energy of the system). It is the reason the interaction occurs.

The supposed interaction in the structures “K-L-M” is expressed in the change of expected values of the “M” fragment spectral parameters. It was postulated by us earlier [2, 3] for *para*-substituted alkylbenzenes by the general formula **3** (including monoalkylbenzenes, where X=H). In the molecules of mentioned compounds the fragment “K” is the alkyl group (Alk) and the fragment “M” includes nuclei of atoms H-2 (H-6), H-3 (H-5), C-1, C-2 (C-6) and C-3 (C-5) of the phenyl ring.

In the second example – phenylsulfones **4** – functional groups X are the fragments “K” and protons H-2, H-3 and H-4 [4, 5] are the fragments “M”. One more example shows aryl-containing methyl and ethyl esters **5**, where protons of alkoxy groups are the fragments “M” and aryl groups (Ar) are the fragments “K” [6, 7].



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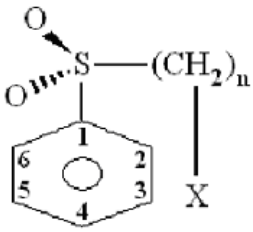

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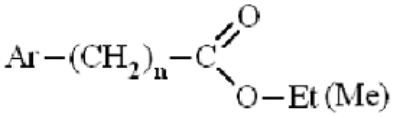

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The same but not described earlier deviations from the anticipated values of δ^H parameters in the NMR ^{1}H spectra we also observed for ethers, acetales, alcohols, saturated alkanes, etc. The variety of compounds for which the described phenomenon takes place allows us to assume that **the observed results are widely spread** and **may be general for all classes of compounds**.

As a result of interaction between "K" and "M" molecule fragments in the conformation **2** the changes in spectral parameters of the fragment "K" should be expected beside the described changes in spectral parameters of the fragment "M". Hitherto we did not observe such changes. There are several reasons for this fact. One of them is insufficient resolution of spectral lines in available NMR ^{1}H spectra obtained at low-frequency instruments (see below). Thus we were not able to attribute the obtained signals.

But the main reason was choice of logically-founded "expected" [7] spectral parameter necessary to compare it with experimental value. In this paper we describe the mentioned problems and ways of their solving as well as the obtained results.

To prove the existence of changes in spectral parameters of the fragment "K" the structures of *para*-substituted propylbenzenes **6 – 16** (where R, R^1= H, CH_3) are the most suitable to our mind. This substances is the part of mort wide class of alkylbenzene compounds pictured by the general formula **3**.

$$p\text{-X-C}_6\text{H}_4\text{-CRR}^1\text{-CH}_2\text{-CH}_3$$

6 - 16

We intend to prove the presence of disturbance of chemical shifts of alkyl fragment methyl end-groups compared with their expected values. With this aim we give in the table chemical shifts of methyl end-groups which are parts of ethyl fragment of the following compounds. Monoalkylbenzenes: propylbenzene **6**, sec-butylbenzene **7**, tert-amylbenzene **8** and 3-phenylpentane **24**. *Para*-alkylphenols: 4-propylphenol **9**, 4-(sec-butyl)phenol **10** and its acetate **16**, as well as 4-(*tert*-amyl)phenol **11**. Data of NMR ^{1}H spectra of other propylbenzenes and sec-butylbenzenes are given for the comparison: *para*-propylaniline **12**, *para*-sec-butylaniline **13**, *para*-nitro-(sec-butyl)benzene **14**, *para*-(sec-butyl)anizol **15** and the simplest unbranched and branched alkanes: *n*-pentane **17**, 2-methylbutane **18**, 3-methylpentane **19**, 3-methylhexane **20**, 2,2-dimethylbutane **21**, 3,3-dimethylpentane **22** and 3,3,-dimethyloctane **23**. Some data of NMR ^{1}H spectra of some alkanes, haloid alkyls, alcohols and their derivatives (esters and ethers) without numbering are also involved in the discussion.

2. Experimental

Introduced designations and informational sources. Basic spectral parameters of methyl end-groups are denoted as $\delta_{CH3}^{H,\mathbf{N}}$. The superscript contains type of spectra ("H" – protonic) and number of compound by bold (**N**). Sometimes there is the number of informational source in square brackets, *e.g.* $\delta_{CH3}^{H,\mathbf{6}[9]}$ (chemical shift of propylbenzene methyl group protons taken from the spectrum given in [9]). The subscript denotes three hydrogen atoms of methyl end-group, spectrum of which is investigated.

Selection of spectral data sources is based on their reliability and compatibility, criteria of which are discussed in [8]. We used the values of basic spectral parameters $\delta_{CH3}^{H,\mathbf{N}[9]}$ and $\delta_{CH3}^{H,\mathbf{N}[10]}$ obtained in deuterochloroform as a solvent and taken from informational sources [9] and [10]. The use of $CDCl_3$ as a solvent is grounded earlier [3, 4], therefore spectra obtained in other solvents (for example CCl_4 or DMSO-d_6) are not discussed here.

Signals attribution in NMR ^{1}H spectra. In all cases in [9] there is author's attribution of spectral signals to the corresponding values of $\delta_{CH3}^{H,\mathbf{N}[9]}$. Since in [10] the attribution of triplet signals of corresponding methyl groups is absent, we attributed them by ourselves. Usually the values of $\delta_{CH3}^{H,\mathbf{N}[9]}$ and $\delta_{CH3}^{H,\mathbf{N}[10]}$ parameters are in a good agreement between each other and the difference between them is less than 0.020 ppm. The latter is accepted by us as average possible experimental error (measurements accuracy), *i.e.* accuracy of $\delta_{CH3}^{H,\mathbf{N}}$ parameters determination.

Basic spectral parameters $\delta_{CH3}^{H,\mathbf{N}[9]}$ given in [9] were obtained using instruments with different frequency: low-frequency instrument (90 MHz) and high-frequency instrument (300 or 400 MHz). In those cases when two different values of $\delta_{CH3}^{H,\mathbf{N}[9]}$ are given in [9], we used the value obtained at high-frequency instrument. To our mind the most reliable are basic spectral parameters $\delta_{CH3}^{H,\mathbf{N}[10]}$ obtained at the instrument with frequency of 300 MHz and $\delta_{CH3}^{H,\mathbf{N}[9]}$ parameters obtained at the instrument with frequency of 400 MHz. The values of parameters of both types (experimental basic $\delta_{CH3}^{H,\mathbf{N}}$ and calculated differential $\Delta\delta_{CH3}^{H,\mathbf{N}}$, see below) are given with the accuracy of 0.001 ppm.

Besides basic spectral parameters $\delta_{CH3}^{H,\mathbf{N}[10]}$ and $\delta_{CH3}^{H,\mathbf{N}[9]}$ so called "experimental" differential spectral parameters [7] are represented in the Table. They were calculated in accordance with the formula given below. Also for the methyl group there are "expected values" of basic spectral parameter W and "expected values" of differential spectral parameters $\Delta W^{[9]}$ and $\Delta W^{[10]}$. The definitions of all parameters are given below.

Table

Basic and differential spectral parameters of methyl end-groups in compounds 6 – 24

No. of comp	Structural formula (the investigated methyl group is marked)	$\delta_{\alpha\text{-}B}^{H,N[10]}$, ppm	$\delta_{\alpha\text{-}B}^{H,N[9]}$, ppm	$\Delta\delta_{\alpha\text{-}B}^{H,N[10]}$, ppm	$\Delta\delta_{\alpha\text{-}B}^{H,N[9]}$, ppm	W, ppm	$\Delta W^{[10]}$, ppm	$\Delta W^{[9]}$, ppm
6	C_6H_5-CH_2-CH_2-C***H₃***	0.930	0.940	+0.050	+0.056	1.00	**-0.070**	**-0.060**
7	C_6H_5-CH(CH_3)-CH_2-C***H₃***	0.820	0.820	**-0.040**	**-0.040**	1.00	**-0.180**	**-0.180**
8	C_6H_5-C(CH_3)$_2$-CH_2-C***H₃***	-	0.690	-	**-0.100**	1.00	**-**	**-0.310**
9	*p*-HO-C_6H_4-CH_2-CH_2-C***H₃***	0.910	0.918	+0.030	+0.034	1.00	**-0.090**	**-0.082**
10	*p*-HO-C_6H_4-CH(CH_3)-CH_2-C***H₃***	-	0.810	**-**	**-0.050**	1.00	**-**	**-0.190**
11	*p*-HO-C_6H_4-C(CH_3)$_2$-CH_2-C***H₃***	0.660	0.680	**-0.130**	**-0.110**	1.00	**-0.340**	**-0.320**
12	*p*-H_2N-C_6H_4-CH_2-CH_2-C***H₃***	0.910	0.902	+0.030	+0.018	1.00	**-0.090**	**-0.098**
13	*p*-H_2N-C_6H_4-CH(CH_3)-CH_2-C***H₃***	0.800	-	**-0.060**	**-**	1.00	**-0.200**	**-**
14	*p*-O_2N-C_6H_4-CH(CH_3)-CH_2-C***H₃***	-	0.833	**-**	**-0.027**	1.00	**-**	**-0.167**
15	*p*-H_3C-O-C_6H_4-CH(CH_3)-CH_2-C***H₃***	-	0.804	**-**	**-0.056**	1.00	**-**	**-0.196**
16	*p*-Ac-O-C_6H_4-CH(CH_3)-CH_2-C***H₃***	-	0.812	**-**	**-0.048**	1.00	**-**	**-0.188**
17	C***H₃***-CH_2-CH_2-CH_2-C***H₃***	0.880	0.884	0.000	0.000			
18	CH_3-CH(CH_3)-CH_2-C***H₃***	0.860	0.865	0.000	+0.005			
19	C***H₃***-CH_2-CH(CH_3)-CH_2-C***H₃***	0.860	-	0.000	-			
20	C***H₃***-CH_2- CH_2-CH(CH_3)-CH_2-C***H₃***	0.860	0.857	0.000	-0.003			
21	CH_3-C(CH_3)$_2$-CH_2-C***H₃***	0.820	0.840	+0.030	+0.050			
22	CH_3-CH_2-C(CH_3)$_2$-CH_2-C***H₃***	0.790	0.792	0.000	+0.002			
23	CH_3- (CH_2)$_4$-C(CH_3)$_2$-CH_2-C***H₃***	-	0.789	-	-0.001			
24	C_6H_5-CH(CH_2- C***H₃***)$_2$	-	0.77	-	**-0.090**		**-0.230**	

3. Results and Discussion

The comparison of basic spectral parameters $\delta_{Me}^{H,N}$ of methyl groups protons (given by italic as C*H₃* in the formulas presented in the Table) was carried out by two ways. In the first, more obvious but less strict case we partially used virtual values W. In the second, more strict but less obvious case we used only experimental data.

3.1. Introduced Terms

The most obvious criterion of the presence of assumed interaction between unbound fragments "K" and "M" in the molecules of investigated alkylbenzenes **6-16** is the definite systematic deviations of experimental values (δ_{exp}^{H}) from their anticipated (expected) values δ_{ant}^{H} = W. For quantitative comparison of such deviations we introduced virtual differential parameters ΔW ($\Delta W = \delta_{exp}^{H} - \delta_{ant}^{H}$, *i.e.* δ_{exp}^{H} - W).

To our mind, another set of experimental differential spectral parameters is more rigid. We denoted them as $\Delta\delta_{CH3}^{H,\mathbf{N}}$. Such parameters are calculated as a difference between experimental values: $\Delta\delta_{CH3}^{H,\mathbf{N}} = \delta_{CH3}^{H,\mathbf{N}} - \delta_{CH3}^{H,stand.}$. The latter value is the corresponding basic spectral parameter $\delta_{Me}^{H,stand}$ of the compound taken by us as a standard. The advantage of this set of differential parameters is using of only experimental values for the calculations. The main disadvantage is the absence of evident physical meaning.

<u>Differential "experimental" spectral parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$</u>. As an example we calculate $\Delta\delta_{CH3}^{H}$ for propylbenzene (**6**): $\Delta\delta_{CH3}^{\mathbf{H6}[10]} = \delta_{CH3}^{\mathbf{H6}[10]} - \delta_{CH3}^{\mathbf{H17}[10]}$ = 0.930 – 0.880 = +0.050 ppm. The subtrahend is corresponding "standard" compound which is *n*-pentane (**17**) here. To calculate the differential "experimental" parameters of other compounds it is advisable to use other substances as standards depending on their structures.

<u>"Anticipated values" of basic spectral parameters</u> are virtual evaluation values. We denote them as capital Latin letters $W^{\mathbf{N}}$, *e.g.* $W^{\mathbf{6}}$. The numerical values of $W^{\mathbf{N}}$ parameters are approximate and debatable. They are equal to those assumed values of chemical shifts of methyl groups protons which would be in a case of absence of interaction of unbound fragments "K" and "M" in the molecules of investigated compounds. Therefore under the term of "anticipated value" we mean logically grounded virtual value of the basic spectral parameter $W^{\mathbf{N}}$, *i.e.* the non-existent value of the signal we are interested in and which we would expect to see in NMR ^{1}H spectrum.

<u>"Anticipated values" of differential spectral parameters,</u> which we also call as virtual parameters, are calculated evaluation values. They are denoted by symbol "ΔW", *e.g.* $\mathbf{\Delta}W^{\mathbf{N}}$. It is the difference between experimental basic parameter δ_{CH3}^{H} and virtual anticipated parameter W, *e.g.* $\Delta W^{\mathbf{6}} = \delta^{\mathbf{H6}} - W^{6}$.

3.2.Criteria of the Presence of Supposed Interaction between Unbound Fragments "K" and "M" in the Molecules of Investigated Compounds

Earlier [7] we selected three main criteria:

1. Negative values of virtual differential parameters ΔW. The larger values the stronger interaction.

2. If the absolute values of ΔW parameters are close to zero, the founded assumptions about the presence or absence of mentioned interaction are maid with difficulty.

3. The negative values of "experimental" differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$. The larger absolute value of the negative parameter the stronger supposed interaction.

Therefore, negative values of differential parameters ΔW and $\Delta\delta_{CH3}^{H,\mathbf{N}}$ are given by bold in the Table by greater size.

3.3. Basis of Principles of Standard Compounds Choice

In above-mentioned example of "experimental" differential parameter calculation for propylbenzene **6** pentane **17** is chosen as a standard compound. Such a choice is explained by the following:

1. To compare NMR ^{1}H spectra of alkylbenzenes **6-16** and **24** we choose as a standard compound just the simplest alkanes, absorption of which takes place in the highest field.
2. It is necessary the standard compound would contain the same alkyl fragment in the molecule as a comparable alkylbenzene **6-16**, **24**. Thus in a case of propylbenzenes **6, 9, 12** and **24** such fragment is *n*-propyl radical -CH_2-CH_2-C***H₃***; in a case of sec-butylbenzenes **7, 10** and **13-16** – sec-butyl radical -CH(CH_3)-CH_2-C***H₃*** and for *tert*-amylbenzenes **8** and **11** – *tert*-amyl radical -C(CH_3)$_2$ -CH_2-C***H₃***.

The simplest alkane containing *n*-propyl radical -CH_2-CH_2-C***H₃*** is propane which is gaseous under usual conditions. Its formula differs from the formulas of investigated propylbenzenes **6,9** and **12** by hydrogen atom instead of aryl fragment. The next homolog (*n*-butane, which is also gaseous compound) contains methyl group instead of aryl group. The NMR^{1}H spectra of both compounds in $CDCl_3$ are absent in [9, 10], therefore we could not use them as standard compounds. The next homolog is liquid *n*-pentane **17** which contains ethyl group instead of aryl one attached to the propyl radical. Its NMR^{1}H spectrum is given in both [9] and [10], therefore we can use it as a standard. In accordance with above-mentioned isopentane **18** and 3-methylpenane **19** may be standard compounds for sec-butylbenzenes **7, 10** and **13-16** and 2,2-dimethylbutane **21** and 3,3-dimethylpentane **22** – for *tert*-amylbenzenes.

3.3.1. Statistic basis of chosen standard values $\delta_{CH3}^{H,st.}$

We chose compounds **17, 19** and **22** as standard compounds. In all of them investigated radical is attached to the ethyl group. To create the statistic reliability we compared $\delta_{CH3}^{H,st.}$ values with the similar parameters of the nearest homologs in which methyl or *n*-propyl or longer alkyl groups are attached to the radical instead of ethyl group.

In accordance with above-mentioned definition pentane **17** for which $\delta_{CH3}^{H,st.}$ = 0.880 ppm should be a standard compound for *n*-propyl radical (CH_3-CH_2- + -CH_2-CH_2-C***H₃***). 3-Methylpentane **19** (CH_3-CH_2- + -CH(CH_3)-CH_2-C***H₃***), for which $\delta_{CH3}^{H,st.}$ = 0.860 ppm should be the standard for sec-butyl radical. 3,3-Dimethylpentane **22** (CH_3-CH_2- + -C(CH_3)$_2$-CH_2-C***H₃***), for which $\delta_{CH3}^{H,st.}$ = 0.790 ppm is the standard for *tert*-amyl radical.

The "statistic basis" of the chosen standard value $\delta_{CH3}^{H,st.}$ is ensured by isopentane **18** (CH_3- + -CH(CH_3)-CH_2-C***H₃***), for which values $\delta_{CH3}^{H,\mathbf{18}[10]}$ = 0.860 ppm and $\delta_{CH3}^{H,\mathbf{18}[9]}$ = 0.865 ppm are given in the Table. This value for sec-butyl radical is from the direction of methyl radical which is smaller than ethyl one. From the direction of larger radicals 3-methylhexane **20** (CH_3-CH_2-CH_2- + -CH(CH_3)-CH_2-C***H₃***) is a standard compound: $\delta_{CH3}^{H,\mathbf{20}[10]}$ = 0.860 ppm and $\delta_{CH3}^{H,\mathbf{20}[9]}$ = 0.857 ppm. All given values "statistically ground" the chosen standard value of 0.860 ppm for all sec-butyl containing compounds **7**, **10** and **13-16**.

The same logic was used for "statistic basis" of standard value for *tert*-amyl containing compounds **8** and **11**. However here we met unanticipated problems. In the literature sources [9, 10] we found 3,3-dimethyloctane **23** is a single homolog of 3,3-dimethylpentane **22** from the direction of "large" radicals. Its $\delta_{CH3}^{H,\mathbf{23}\,[9]}$ value equals to 0.789 ppm. It is practically the same as $\delta_{CH3}^{H,\mathbf{22}\,[10]}$ = 0.790 ppm and $\delta_{CH3}^{H,\mathbf{22}\,[9]}$ = 0.792 ppm of the "standard" compound **22**. At the same time for 2,2-dimethylbutane **21** (homolog from the direction of "smaller" methyl group) the values of basic parameter $\delta_{CH3}^{H,\mathbf{21}}$ are essentially higher and equal to: $\delta_{CH3}^{H,\mathbf{21}\,[10]}$ = 0.820 ppm and $\delta_{CH3}^{H,\mathbf{21}\,[9]}$ = 0.840 ppm.

Therefore the choice of $\delta_{CH3}^{H,st.}$ = 0.790 ppm is grounded by two arguments one of which we used earlier [11]. "Short-chain" methyl group is the first in the homologous row of alkyl groups and that is why it may differ from "typical long-chain" alkyl groups (*n*-butyl and higher). Ethyl and *n*-propyl groups are intermediate ones between "short-chain" methyl groups and "long-chain" alkyl groups. But the spectral properties investigated in [11] allow to suppose that "intermediate" ethyl an *n*-propyl groups are closer to "long-chain" groups. As it is shown above, the same situation is observed for *tert*-amyl containing alkanes **21, 22** and **23**. This argument supports the choice of value $\delta_{CH3}^{H,st.}$= 0.790 ppm instead of $\delta_{CH3}^{H,st.}$= 0.830 ppm (as arithmetical mean value between $\delta_{CH3}^{H,\mathbf{21}\,[10].}$ = 0.820 ppm and $\delta_{CH3}^{H,\mathbf{21}\,[9].}$ = 0.840 ppm for "short-chain" 2,2-dimethylbutane **21**).

The second argument. In our opinion the replacement of "short-chain" methyl group for aryl fragment (*i.e.* the transfer from the compound **21** to the compounds **8** and **11**) would lead to more essential changes than replacement of "middle-chain" ethyl group in **22** and especially of "long-chain" pentyl group in **23**. Therefore the value $\delta_{CH3}^{H,st.}$ = 0.790 ppm is more preferable than $\delta_{CH3}^{H,st.}$ = 0.830 ppm as a standard parameter for *tert*-amyl containing compounds.

The same argument was used for choice of standard parameter for *n*-propyl containing compounds **6, 9** and **12** ($\delta_{CH3}^{H,st.}$ = 0.880 ppm). Moreover, for methyl homolog – *n*-butane – the data of NMR ^{1}H spectra in $CDCl_3$ were absent in the literature. The values of δ_{CH3}^{H} = 0.870–0.880 ppm are typical for all "long-chain" nonbranched alkanes.

3.4. Comparison of "Experimental" Differential Parameters $\Delta\delta_{CH3}^{H,N}$ of Alkylbenzenes 6-16 and 24

For *n*-propyl containing compounds the following positive values of differential parameters $\Delta\delta_{CH3}^{H,N}$ are given in the Table: $\Delta\delta_{CH3}^{H,\mathbf{6}[10]}$ = +0.050 ppm and $\Delta\delta_{CH3}^{H,\mathbf{6}[9]}$ = +0.056 ppm for *n*-propylbenzene **6**; $\Delta\delta_{CH3}^{H,\mathbf{9}[10]}$ = +0.030 ppm and $\Delta\delta_{CH3}^{H,\mathbf{9}\,[9]}$ = +0.034 ppm for *para-n*-propylphenol **9** and $\Delta\delta_{CH3}^{H,\mathbf{12}[10]}$ = +0.030 ppm and $\Delta\delta_{CH3}^{H,\mathbf{12}\,[9]}$ = +0.018 ppm for *para-n*-propylaniline **12.** In accordance with earlier accepted definitions [3-5, 7] the given positive values of differential parameters are considered as "relatively small".

Therefore due to the third criterion of the presence or absence of intermolecular interaction between unbound fragments it is probable that the interaction between methyl group of propyl fragment and hydrogen atoms of aryl fragment does not exist or has small value in the investigated *n*-propyl containing compounds **6, 9** and **12.**

On the contrary, for sec-butylbenzenes **7, 10** and **13-16** the negative values of differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ are given in the Table: $\Delta\delta_{CH3}^{H,\mathbf{7}[10]}$ = -0.040 ppm and $\Delta\delta_{CH3}^{H,\mathbf{7}[9]}$ = -0.040 ppm for sec-butylbenzene**7**; $\Delta\delta_{CH3}^{H,\mathbf{10}[9]}$ = -0.050 ppm for *para-(*sec-butyl)phenol **10**, and $\Delta\delta_{CH3}^{H,\mathbf{13}[10]}$ = -0.060 ppm for *para*-(sec-butyl)aniline **13**; $\Delta\delta_{CH3}^{H,\mathbf{14}[9]}$ = -0.027 ppm for *para*-nitro-(sec-butyl)benzene**14**, $\Delta\delta_{CH3}^{H,\mathbf{15}[9]}$ = -0.056 ppm for para-(sec-butyl)anisole **15** and $\Delta\delta_{CH3}^{H,\mathbf{16}[9]}$ = -0.048 ppm for *para*-(sec-butyl)phenol acetate **16**. The absolute values of given negative differential parameters are considered as "relatively small".

In contrast to *n*-propylaryl compounds **6, 9** and **12**, the presence of negative by sign differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ in the isobutyl fragment -CH(CH_3)-CH_2-C***H₃*** assumes the interaction between ethyl group of sec-butyl fragment and aryl ring in the molecules of compounds **7, 10** and **13-16**, as well as **24** (which also may be attributed to this group of compounds).

The more impressive results were obtained during investigations of differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ for *tert*-amylbenzenes **8** and **11**. The negative values of differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ are given in the Table: $\Delta\delta_{Me}^{H,\mathbf{8}[9]}$ = -0.100 ppm for *tert*-amylbenzene **8**; as well as $\Delta\delta_{CH3}^{H,\mathbf{11}[10]}$ = -0.130 ppm and $\Delta\delta_{CH3}^{H,\mathbf{11}[9]}$ = -0.110 ppm for *para-tert*-amylphenol **11**. The absolute values of given negative differential parameters are considered as "considerable" [7].

The presence of considerable by value and negative by sign differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ calculated for the protons of methyl end-group in -C(CH_3)$_2$-CH_2-C***H₃*** allow to sustain that the interaction between methyl group of *tert*-amyl fragment and aryl ring occurs in the molecules of the compounds **8** and **11**.

3.5. Evaluation of Anticipated (Virtual) Basic Spectral Parameters W

We had a complicated task – to ground logically the suggested virtual values of W parameters for the compounds **6-16**.

Earlier [7] we showed that values of W parameters depend mainly on the presence or absence of functional groups in the molecule structure. The presence of electron-attractive substituents shifts the W parameter toward low field and *vice versa*. Comparing the experimental values of basic spectral parameters $\delta_{CH3}^{H,\mathbf{N}}$ in substituted and unsubstituted compounds for three types of alkylbenzenes: propylbenzenes **6, 9, 12**; sec-butylbenzenes **7, 10, 13-16** and *tert*-amylbenzenes **8, 11** one can see that in all cases the substituents act accordingly to above-mentioned principle. For example, in most cases of sec-butylbenzenes the electron-donating substituents (OH in **10**, OMe in **15**, OAc in **16** and NH_2 in **13**) cause the methyl group absorption in higher field and electron-accepting nitrogroup – in lower field compared with unsubstituted sec-butylbenzene**7**. The maximal difference between values of basic spectral parameters is 0.033 ppm ($\delta_{CH3}^{H,N,\mathbf{14}}$ = 0.833 ppm against $\delta_{CH3}^{H,N,\mathbf{13}}$ = 0.800 ppm). Therefore it is necessary to take into account the influence of substituent in phenyl ring while choosing the values of virtual parameters W.

The value of W parameter shows how much (in our opinion) the absorption of methyl end-group in alkylbenzenes **6-16** would be changed compared with that in *n*-alkanes **17, 19, 22** (which were chosen as standard compounds) while exchange of ethyl group for aryl one. Obviously, due

to the stronger electron-accepting influence of aryl group (compared with ethyl group) in alkylbenzenes **6-16** the shift of $\delta_{CH3}^{H,\mathbf{N}}$ values toward low field should take place. However we have not grounded suggestions concerning the value of such shift. Earlier in [7] we assumed that electron-accepting action of phenyl fragment is comparable with the action of iodine or bromine atoms as substituents. Therefore we investigated the values $\delta_{CH3}^{H,\mathbf{N}}$ given in [9, 10] for the row of 1-haloidpropanes, 2-haloidbutanes and 2-haloid-2-methylbutanes, where bromine, iodine and chlorine atoms were used as halogens. Regardless of the type of halogen atom and structure of alkyl radical in haloid alkyl, the values of all founded parameters δ_{Me}^{H} are within the range from 0.90 to 1.10 ppm. The values δ_{Me}^{H} in the corresponding alcohols, esters and ethers have the same order of magnitude. Thus, it was advisable to accept the value of W parameters equal to 1.00 ppm for all compounds **6-16** irrespective of the aryl group structure. Taking into account the greater uncertainty committed while choice of the value W, we do not take into account the less by value differences concerning the influence of substituents in phenyl ring, as well as the presence or absence of methyl groups in *n*-propyl fragment of these compounds.

Then the negative values of virtual differential parameters ΔW were calculated for *n*-propyl containing compounds. They are represented in the Table: $\Delta W^{\mathbf{6}[10]}$ = -0.070 ppm and $\Delta W^{\mathbf{6}[9]}$ = -0.060 ppm for *n*-propylbenzene**6**; $\Delta W^{\mathbf{9}[10]}$ = -0.090 ppm and $\Delta W^{\mathbf{9}[9]}$ = -0.082 ppm for *para-(n*-propyl)phenol **9;** $\Delta W^{\mathbf{12}[10]}$ = -0.090 ppm and $\Delta W^{\mathbf{12}[9]}$ = -0.098 ppm for *para-(n*-propyl)aniline **12**.

Taking into account the above-mentioned peculiarities of the choice of virtual parameters W we extended the uncertainty interval for ΔW by sign and value from -0.100 ppm to +0.100 ppm. In spite of the considerable negative values of differential parameters $\Delta W^{\mathbf{N}}$ for *n*-propyl containing compounds, they found themselves in this interval. Hence, parameters ΔW^{N} can not be considered applicable to determine the absence or presence of intermolecular interaction between unbound molecule fragments in *n*-propyl containing compounds. The cautious conclusion may be done that the interaction between methyl group of propyl fragment and aryl fragment atoms in the compounds **6, 9, 12** does not occur or it is very small.

On the contrary, the large negative values of differential parameters $\Delta W^{\mathbf{N}}$ are represented in the Table for sec-butylbenzenes **7, 10** and **13-16, 24**: $\Delta W^{\mathbf{7}[10]}$ = -0.180 ppm and $\Delta W^{\mathbf{7}[9]}$ = -0.180 ppm for sec-butylbenzene **7**; $\Delta W^{\mathbf{10}[9]}$ = -0.190 ppm for *para*-(sec-butyl)phenol **10**, as well as $\Delta W^{\mathbf{13}[10]}$ = -0.200 ppm for para-(sec-butyl)aniline **13**; $\Delta W^{\mathbf{14}[9]}$ = -0.167 ppm for para-nitro-(sec-butyl)benzene **14**, $\Delta W^{\mathbf{15}[9]}$ = -0.196 ppm for para-(sec-butyl)anisole **15,** $\Delta W^{\mathbf{16}[9]}$ = -0.188 ppm for *para*-(sec-butyl)phenol acetate **16** and $\Delta W^{\mathbf{24}[9]}$ = -0.230 ppm for 3-phenylpentane **24**. The absolute values of differential parameters ΔW are considerable and exceed the limit of accepted interval (0.100 ppm).

Therefore, in contrast to *n*-propyl compounds **6, 9, 12,** the presence of considerable negative differential parameters $\Delta\delta_{CH3}^{H,\mathbf{N}}$ and virtual parameters ΔW calculated for the protons of methyl end-group in $-CH(CH_3)-CH_2-C\underline{\boldsymbol{H_3}}$ allows to assume that the interaction between end-methyl group of sec-butyl fragment and aryl fragment atoms occurs in the compounds **7, 10, 13-16**.

More impressive results were obtained during investigations of virtual differential parameters ΔW for *tert*-amylbenzenes **8** and **11**. Very large negative values of ΔW parameters are represented in the Table. The exceed 0.300 ppm: $\Delta W^{\mathbf{8}[9]}$ = -0.310 ppm for *tert*-amylbenzene **8**; as well as $\Delta W^{\mathbf{11}[10]}$ = -0.340 ppm and $\Delta W^{\mathbf{11}[9]}$ = -0.320 ppm for *para*-(*tert*-amyl)phenol **11**.

The presence of very large negative differential parameters $\Delta\delta_{CH3}^{H,N}$ and ΔW^{N}, calculated for the protons in methyl end-group in $-C(CH_3)_2-CH_2-C\underline{\boldsymbol{H_3}}$ allow to assert that the strong interaction between methyl group of *tert*-amyl fragment and aryl ring occurs in the compounds **8** and **11**.

Thus, both "experimental" and "virtual" differential parameters of alkylbenzenes **7, 10** and **13-16** containing sec-butyl alkyl group and particularly compounds **8** and **11** containing *tert*-amyl fragment meet all criteria concerning the presence of intermolecular influence of phenyl ring through the space on methyl end-group of alkyl fragment.

Taking into account that we postulated earlier [2, 3] the same influence of alkyl groups on phenyl ring (on its *ortho*-protons and carbon atoms C-1 and C-2[1] in particular), we may point to reciprocal influence of molecule fragments which are unbound by chemical bonds between each other. The circle is enclosed.

The reciprocal influence most likely may be realized through the space, for example in "bent" conformation of *tert*-amylbenzene **8** (or *tert*-amylphenol **11**) represented in Fig. 4. The conformations **1** and **2** (where X = H, Alk = $CRR^1CH_2CH_3$ and R^1, R^2 = H or CH_3) are schematically represented in Fig. 3 and 4 respectively. Just by "partial"[2] influence of the system consisting of 6 annular π-electrons of phenyl ring on the distant methyl group of *tert*-amyl fragment (hydrogen atoms of which are circled) we explain the unique by value shift of its protons toward the high yield (till value $\delta_{CH3}^{H} < 0.70$ ppm).

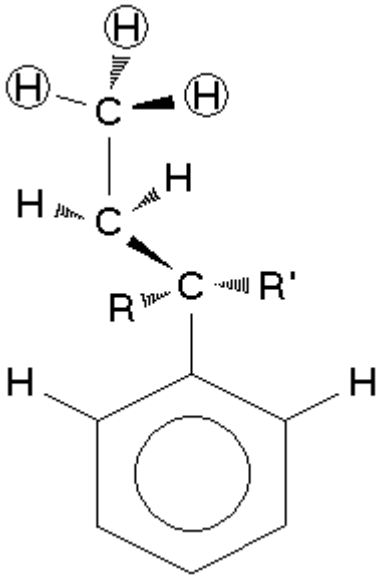

Fig. 3

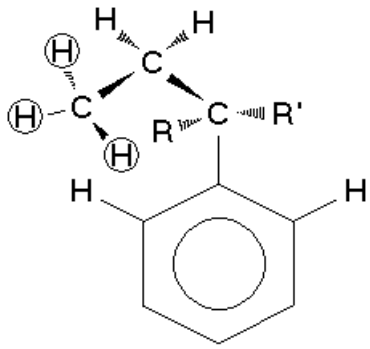

Fig. 4

[1] The spectral changes in specially fitted pairs of compounds indicate such interaction. For instance, the difference between chemical shifts of the analogous atoms of phenyl ring (differential parameters $\Delta\delta_i$) for the pair of compounds *tert*-amylbenzene **8** – *tert*-butylbenzene equal to [3]: for *ortho*-hydrogen atoms $\Delta\delta_o^H$ = -0.075 ppm; for *ipso*-carbon atom of the ring $\Delta\delta_1^C$ = -1.60 ppm; for *ortho*-carbon atoms $\Delta\delta_2^C$ = +0.75 ppm. Almost the same values of differential parameters were calculated for the pair *tert*-amylphenol **11** – *tert*-butylphenol: $\Delta\delta_o^H$ = -0.070 ppm; $\Delta\delta_1^C$ = -1.70 ppm; $\Delta\delta_2^C$ = +0.70 ppm. Differential parameters of smaller absolute value (but with the same signs) were determined for six pairs of the compounds of the type *para*-substituted sec-butylbenzene – *para*-substituted cumene (where hydrogen atom is included to the number of substituents; the average values of differential parameters equal to: $\Delta\delta_o^H$ = -0.049 ppm; $\Delta\delta_1^C$ = -1.17 ppm; $\Delta\delta_2^C$ = +0.62 ppm), as well as for six pairs of the compounds of the type *para*-substituted propylbenzene – *para*-substituted ethylbenzene (average values equal to: $\Delta\delta_o^H$ = -0.021ppm; $\Delta\delta_1^C$ = -1.56 ppm; $\Delta\delta_2^C$ = +0.61 ppm).

[2] For "complete" influence of annular π-electrons of phenyl ring on nearby protons gotten under its influence the shift toward high field is typical. Its value achieves -10 ppm.

On the contrary, in the linear conformation **1** (Fig. 1) such interaction, to our mind, is impossible. We may assume that the same linear conformation given in Fig. 3 is more typical for *n*-propylbenzenes **6, 9** and **12** (where R^1=R^2=H), though it is impossible to exclude for them some interaction in "bent" conformation (Fig. 4, R^1=R^2=H).

4. Conclusions

The data of NMR ^{1}H spectra for alkylbenzenes containing sec-butyl and *tert*-amyl alkyl groups allow to assume the presence of reciprocal influence of aryl ring and distant methyl groups of alkyl fragment taken place during registration of the spectrum. Since both fragments are unbound between each other by chemical bonds we conclude that interaction takes place through the space. The "bent" conformation (Fig. 4) is given as an example, in which the mentioned interaction is the most obvious.

Acknowledgements

The work is fulfilled in the frame of state budget project "Detection of general regularities determining the value of chemical shift in NMR ^{1}H and ^{13}Cspectra depending upon the chemical structure of organic substances", theme # B802-2010.

We acknowledge National Institute of Advanced Science and Technology (SDBS Web://:riodb 01.ibase.aist.go.jp/sdbs) for the given in the article NMR^{1}H spectra.

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