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

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**Abstract.** The chemical shifts in NMR  $^1\text{H}$  spectra of the *para*-substituted propylbenzenes of the general formula:  $p\text{-X-C}_6\text{H}_4\text{-CRR}^1\text{CH}_2\text{CH}_3$  (where R,  $\text{R}^1 = \text{H}, \text{CH}_3$ ) have been analyzed. The presence or absence of the aryl fragment influence on the methyl end-group was observed by the value of the basic spectral parameters – the chemical shifts of methyl protons ( $\delta_{\text{CH}_3}^{\text{H}}$ ) in comparison with analogous data of corresponding alkanes. The specific criteria for identifying such effect were developed and validated. We make the overall conclusion about high probability of the reciprocal intramolecular interactions between unbound fragments of the molecule in *tert*-amylbenzene and *tert*-amylphenol ( $\text{R} = \text{R}^1 = \text{CH}_3$ ).

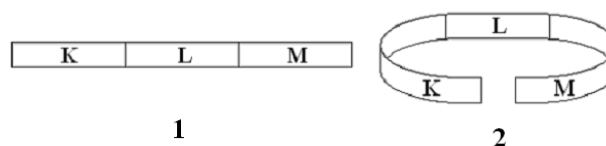
**Keywords:** NMR  $^1\text{H}$  spectra, *para*-substituted propylbenzenes, spectral parameter, differential parameter, virtual, intramolecular interactions.

### 1. Introduction

While analyzing the peculiarities of NMR  $^1\text{H}$  and  $^{13}\text{C}$  spectra of different classes of organic compounds we suppose that under recording spectra conditions the intramolecular interactions between unbound fragments of the molecule may take place through the space. The existence of the 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 this.

The transition states with curved conformations, the same as **2**, are well-known in the synthetic chemistry, *e.g.* in the reactions of electrophilic cyclization or in substitution reactions proceeding with the transfer of reaction centre. Similar transition state was given in an article [1] describing NMR  $^{17}\text{O}$  spectra of crowded alcohols, where authors postulated through-space interaction in  $\text{CH}_3\cdots\text{O}$ .

We propose the following explanation of the observed phenomenon in accordance with the postulate: “*The possible interaction between two energy states occurs always under 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 a new system occupies a lower energy level (state  $B^1$ ).

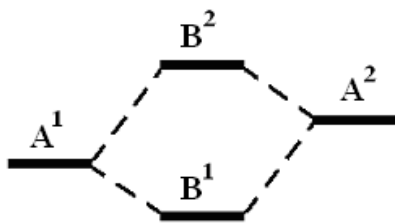
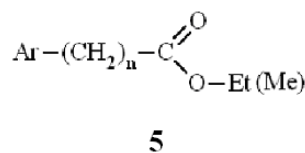
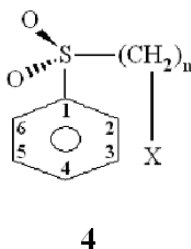
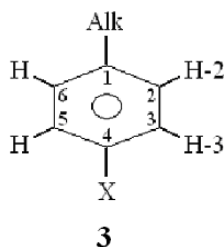


Fig. 2

It is logical 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 that the interaction occurs.



We also observed the same but not described earlier deviations from the anticipated values of  $d^H$  parameters in the NMR  $^1\text{H}$  spectra for ethers, acetals, 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.**

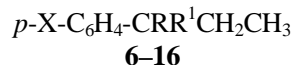
As a result of interaction between “K” and “M” molecule fragments in the conformation **2** the changes in spectral parameters of the fragment “K” should be expected beside the described changes in spectral parameters of the fragment “M”. Hitherto we did not observe such changes. There are several reasons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

But the main reason was the choice of logically-founded “expected” [7] spectral parameter necessary for its comparison with the experimental value. In this paper we describe the mentioned problems and ways of their solving as well as achieving 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<sup>1</sup> = H, CH<sub>3</sub>) are the most suitable to our mind. These compounds are the part of wider class of alkylbenzenes according to the general formula **3**.

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 ethers **5**, where protons of alkoxy groups are the fragments “M” and aryl groups (Ar) are the fragments “K” [6,7].



We intend to prove the presence of methyl end-groups displacement of alkyl fragment chemical shifts compared with their expected values. With this aim in the table we give 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  $^1\text{H}$  spectra of other propylbenzenes and sec-butylbenzenes are given for the comparison: *para*-propylaniline **12**, *para*-sec-butylaniline **13**, *para*-nitro-sec-butylbenzene **14**, *para*-sec-butylanizol **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  $^1\text{H}$  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  $d_{CH_3}^{H,N}$ . The superscript contains the type of spectra (“H” – protonic) and the number of the compound by bold (*N*). Sometimes there is the number of informational source in square brackets, *e.g.*  $d_{CH_3}^{H,6[9]}$  (chemical shift of propylbenzene methyl group from the spectrum given in [9]). The subscript denotes three hydrogen atoms of methyl end-group, the 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  $d_{CH_3}^{H,N[9]}$  and  $d_{CH_3}^{H,N[10]}$  obtained in deuteriochloroform 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  $^1H$  spectra. In all cases in [9] there is the author’s attribution of spectral signals to the corresponding values of  $d_{CH_3}^{H,N[9]}$ . Since in [10] the attribution of triplet signals of corresponding methyl groups is absent, we attributed them by ourselves. Usually the values of  $d_{CH_3}^{H,N[9]}$  and  $d_{CH_3}^{H,N[10]}$  parameters are in good agreement between each other and the difference between them is less than 0.020 ppm. The latter is accep-

ted by us as the average possible experimental error (measurements accuracy), *i.e.* accuracy of  $d_{CH_3}^{H,N}$  parameters determination.

Basic spectral parameters  $d_{CH_3}^{H,N[9]}$  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  $d_{CH_3}^{H,N[9]}$  are given in [9], we used the value obtained on high-frequency instrument. To our mind the most reliable are basic spectral parameters  $d_{CH_3}^{H,N[10]}$  obtained on the instrument with frequency of 300 MHz and  $d_{CH_3}^{H,N[9]}$  parameters obtained on the instrument with frequency of 400 MHz. The values of parameters of both types (experimental basic  $d_{CH_3}^{H,N}$  and calculated differential  $\Delta d_{CH_3}^{H,N}$ , see below) are given with the accuracy of 0.001 ppm.

Besides basic spectral parameters  $d_{CH_3}^{H,N[10]}$  and  $d_{CH_3}^{H,N[9]}$  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)	$\delta_{CH_3}^{H,N[10]}$ , ppm	$\delta_{CH_3}^{H,N[9]}$ , ppm	$\Delta\delta_{CH_3}^{H,N[10]}$ , ppm	$\Delta\delta_{CH_3}^{H,N[9]}$ , ppm	$W$ , ppm	$\Delta W^{[10]}$ , ppm	$\Delta W^{[9]}$ , ppm
6	$C_6H_5-CH_2-CH_2-\underline{CH_3}$	0.930	0.940	+0.050	+0.056	1.00	-0.070	-0.060
7	$C_6H_5-CH(CH_3)-CH_2-\underline{CH_3}$	0.820	0.820	-0.040	-0.040	1.00	-0.180	-0.180
8	$C_6H_5-C(CH_3)_2-CH_2-\underline{CH_3}$	-	0.690	-	-0.100	1.00	-	-0.310
9	$p-HO-C_6H_4-CH_2-CH_2-\underline{CH_3}$	0.910	0.918	+0.030	+0.034	1.00	-0.090	-0.082
10	$p-HO-C_6H_4-CH(CH_3)-CH_2-\underline{CH_3}$	-	0.810	-	-0.050	1.00	-	-0.190
11	$p-HO-C_6H_4-C(CH_3)_2-CH_2-\underline{CH_3}$	0.660	0.680	-0.130	-0.110	1.00	-0.340	-0.320
12	$p-H_2N-C_6H_4-CH_2-CH_2-\underline{CH_3}$	0.910	0.902	+0.030	+0.018	1.00	-0.090	-0.098
13	$p-H_2N-C_6H_4-CH(CH_3)-CH_2-\underline{CH_3}$	0.800	-	-0.060	-	1.00	-0.200	-
14	$p-O_2N-C_6H_4-CH(CH_3)-CH_2-\underline{CH_3}$	-	0.833	-	-0.027	1.00	-	-0.167
15	$p-H_3C-O-C_6H_4-CH(CH_3)-CH_2-\underline{CH_3}$	-	0.804	-	-0.056	1.00	-	-0.196
16	$p-Ac-O-C_6H_4-CH(CH_3)-CH_2-\underline{CH_3}$	-	0.812	-	-0.048	1.00	-	-0.188
17	$\underline{CH_3}-CH_2-CH_2-CH_2-\underline{CH_3}$	0.880	0.884	0.000	0.000			
18	$CH_3-CH(CH_3)-CH_2-\underline{CH_3}$	0.860	0.865	0.000	+0.005			
19	$\underline{CH_3}-CH_2-CH(CH_3)-CH_2-\underline{CH_3}$	0.860	-	0.000	-			
20	$\underline{CH_3}-CH_2-CH_2-CH(CH_3)-CH_2-\underline{CH_3}$	0.860	0.857	0.000	-0.003			
21	$CH_3-C(CH_3)_2-CH_2-\underline{CH_3}$	0.820	0.840	+0.030	+0.050			
22	$CH_3-CH_2-C(CH_3)_2-CH_2-\underline{CH_3}$	0.790	0.792	0.000	+0.002			
23	$CH_3-(CH_2)_4-C(CH_3)_2-CH_2-\underline{CH_3}$	-	0.789	-	-0.001			
24	$C_6H_5-CH(CH_2-\underline{CH_3})_2$	-	0.77	-	-0.090		-0.230	

### 3. Results and Discussion

The comparison of basic spectral parameters  $d_{Me}^{H,N}$  of methyl groups protons (given by italic as  $CH_3$  in the formulas presented in the Table) was carried out by two ways. In the first one (more obvious but less strict case) we partially used virtual values  $W$ . In the second one (more strict but less obvious case) we used only experimental data.

#### 3.1. Introduced Terms

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

To our mind, another set of experimental differential spectral parameters is more rigid. We denoted them as  $\Delta d_{CH_3}^{H,N}$ . Such parameters are calculated as the difference between experimental values:  $\Delta d_{CH_3}^{H,N} = \delta_{CH_3}^{H,N} - \delta_{CH_3}^{H,stand}$ . 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 for calculations only experimental values. The main disadvantage is the absence of evident physical meaning.

Differential “experimental” spectral parameters  $\Delta d_{CH_3}^{H,N}$ . As an example we calculate  $\Delta d_{CH_3}^{H,N}$  for propylbenzene (**6**):  $\Delta d_{CH_3}^{H,N} = \delta_{CH_3}^{H6[10]} - \delta_{CH_3}^{H7[10]} = 0.930 - 0.880 = +0.050$  ppm. The subtrahend is the 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.

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

“Anticipated values” of differential spectral parameters, which we also call as virtual parameters, are calculated evaluation values. They are denoted by the

symbol “ $\Delta W$ ”, e.g.  $\Delta W^N$ . It is the difference between experimental basic parameter  $d_{CH_3}^H$  and virtual anticipated parameter  $W$ , e.g.  $\Delta W^6 = \delta_{CH_3}^{H6} - W^6$ .

#### 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  $\Delta W$ . The larger values the stronger interaction.

2. If the absolute values of  $\Delta W$  parameters are close to zero, the founded assumptions about the presence or absence of the mentioned interaction are made with difficulty.

3. The negative values of “experimental” differential parameters  $\Delta d_{CH_3}^{H,N}$ . The larger absolute value of the negative parameter the stronger the supposed interaction.

Therefore, negative values of differential parameters  $\Delta W$  and  $\Delta d_{CH_3}^{H,N}$  are given in the Table by bold (greater size).

#### 3.3. Substantiation 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  $^1H$  spectra of alkylbenzenes **6–16** and **24** we choose just the simplest alkanes as a standard compound, absorption of which takes place in the highest field.

2. It is necessary that the standard compound should 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 a fragment is *n*-propyl radical  $-CH_2-CH_2-\underline{CH_3}$ ; in a case of sec-butylbenzenes **7**, **10** and **13–16** – sec-butyl radical  $-CH(CH_3)-CH_2-\underline{CH_3}$  and for *tert*-amylbenzenes **8** and **11** – *tert*-amyl radical  $-C(CH_3)_2-CH_2-\underline{CH_3}$ .

The simplest alkane containing *n*-propyl radical  $-CH_2-CH_2-\underline{CH_3}$  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  $^1H$  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<sup>1</sup>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-methylpentane **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 substantiation of chosen standard values $d_{CH_3}^{H,st.}$

We chose compounds **17**, **19** and **22** as standard compounds. In all of them the investigated radical is attached to the ethyl group. To create the statistic reliability we compared  $d_{CH_3}^{H,st.}$  values with the similar parameters of the nearest homologs in which methyl, *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  $\delta_{CH_3}^{H,st.} = 0.880$  ppm should be a standard compound for *n*-propyl radical (CH<sub>3</sub>-CH<sub>2</sub>- + -CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>). 3-Methylpentane **19** (CH<sub>3</sub>-CH<sub>2</sub>- + -CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>), for which  $\delta_{CH_3}^{H,st.} = 0.860$  ppm should be the standard for sec-butyl radical. 3,3-Dimethylpentane **22** (CH<sub>3</sub>-CH<sub>2</sub>- + -C(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>3</sub>), for which  $\delta_{CH_3}^{H,st.} = 0.790$  ppm is the standard for *tert*-amyl radical.

The “statistic substantiation” of the chosen standard value  $\delta_{CH_3}^{H,st.}$  is ensured by isopentane **18** (CH<sub>3</sub>- + -CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>), for which values  $\delta_{CH_3}^{H,18[10]} = 0.860$  ppm and  $\delta_{CH_3}^{H,18[9]} = 0.865$  ppm are given in the Table. This value for sec-butyl radical is from the direction of methyl radical which is smaller than the ethyl one. From the direction of larger radicals 3-methylhexane **20** (CH<sub>3</sub>-CH<sub>2</sub>-CH<sub>2</sub>- + -CH(CH<sub>3</sub>)-CH<sub>2</sub>-CH<sub>3</sub>) is a standard compound:  $\delta_{CH_3}^{H,20[10]} = 0.860$  ppm and  $\delta_{CH_3}^{H,20[9]} = 0.857$  ppm. All given values “statistically ground” the chosen standard value of 0.860 ppm for all sec-butylcontaining compounds **7**, **10** and **13-16**.

The same logic was used for “statistic substantiation” of standard value for *tert*-amylcontaining 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  $\delta_{CH_3}^{H,23[9]}$  value equals to 0.789 ppm. It is practically the same as  $\delta_{CH_3}^{H,22[10]} = 0.790$  ppm and  $\delta_{CH_3}^{H,22[9]} = 0.792$  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  $\delta_{CH_3}^{H,21}$  are essentially higher and equal to:  $\delta_{CH_3}^{H,21[10]} = 0.820$  ppm and  $\delta_{CH_3}^{H,21[9]} = 0.840$  ppm.

Therefore the choice of  $\delta_{CH_3}^{H,st.} = 0.790$  ppm is substantiated 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 and *n*-propyl groups are closer to “long-chain” groups. As it is shown above, the same situation is observed for *tert*-amylcontaining alkanes **21**, **22** and **23**. This argument supports the choice of value  $\delta_{CH_3}^{H,st.} = 0.790$  ppm instead of  $\delta_{CH_3}^{H,st.} = 0.830$  ppm (as arithmetical mean value between  $\delta_{CH_3}^{H,21[10]} = 0.820$  ppm and  $\delta_{CH_3}^{H,21[9]} = 0.840$  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  $\delta_{CH_3}^{H,st.} = 0.790$  ppm is more preferable than  $\delta_{CH_3}^{H,st.} = 0.830$  ppm as a standard parameter for *tert*-amylcontaining compounds.

The same argument was used for choice of standard parameter for *n*-propylcontaining compounds **6**, **9** and **12** ( $\delta_{CH_3}^{H,st.} = 0.880$  ppm). Moreover, for methyl homolog – *n*-butane – the data of NMR<sup>1</sup>H spectra in CDCl<sub>3</sub> were absent in the literature. The values of  $\delta_{CH_3}^H = 0.870$ – $0.880$  ppm are typical for all “long-chain” nonbranched alkanes.

### 3.4. Comparison of “Experimental” Differential Parameters $\Delta\delta_{CH_3}^{H,N}$ of Alkylbenzenes 6–16 and 24

For *n*-propylcontaining compounds the following positive values of differential parameters  $\Delta\delta_{CH_3}^{H,N}$  are given in the Table:  $\Delta\delta_{CH_3}^{H,6[10]} = +0.050$  ppm and  $\Delta\delta_{CH_3}^{H,6[9]} = +0.056$  ppm for *n*-propylbenzene **6**;  $\Delta\delta_{CH_3}^{H,9[10]} = +0.030$  ppm and  $\Delta\delta_{CH_3}^{H,9[9]} = +0.034$  ppm for *para-n*-propylphenol **9**;  $\Delta\delta_{CH_3}^{H,12[10]} = +0.030$  ppm and  $\Delta\delta_{CH_3}^{H,12[9]} = +0.018$  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 intramolecular 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 a small value in the investigated *n*-propylcontaining compounds **6**, **9** and **12**.

On the contrary, for sec-butylbenzenes **7**, **10** and **13-16** the negative values of differential parameters  $\Delta\delta_{CH_3}^{H,N}$  are given in the Table:  $\Delta\delta_{CH_3}^{H,7[10]} = -0.040$  ppm and  $\Delta\delta_{CH_3}^{H,7[9]} = -0.040$  ppm for sec-butylbenzene **7**;  $\Delta\delta_{CH_3}^{H,10[9]} = -0.050$  ppm for *para*-sec-butylphenol **10**, and  $\Delta\delta_{CH_3}^{H,13[10]} = -0.060$  ppm for *para*-sec-butylaniline **13**;  $\Delta\delta_{CH_3}^{H,14[9]} = -0.027$  ppm for *para*-nitro-sec-butylbenzene **14**,  $\Delta\delta_{CH_3}^{H,15[9]} = -0.056$  ppm for *para*-sec-butylanisole **15** and  $\Delta\delta_{CH_3}^{H,16[9]} = -0.048$  ppm for *para*-sec-butylphenol 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  $\Delta\delta_{CH_3}^{H,N}$  in the isobutyl fragment  $-\text{CH}(\text{CH}_3)-\text{CH}_2-\underline{\text{CH}}_3$  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  $\Delta\delta_{CH_3}^{H,N}$  for *tert*-amylbenzenes **8** and **11**. The negative values of differential parameters  $\Delta\delta_{CH_3}^{H,N}$  are given in the Table:  $\Delta\delta_{Me}^{H,8[9]} = -0.100$  ppm for *tert*-amylbenzene **8**; as well as  $\Delta\delta_{CH_3}^{H,11[10]} = -0.130$  ppm and  $\Delta\delta_{CH_3}^{H,11[9]} = -0.110$  ppm for *para*-*tert*-amylphenol **11**. The absolute values of given negative differential parameters are considered as “considerable” ones [7].

The presence of considerable by value and negative by sign differential parameters  $\Delta\delta_{CH_3}^{H,N}$  calculated for the protons of methyl end-group in  $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\underline{\text{CH}}_3$  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 substantiate logically the suggested virtual values of  $W$  parameters for the compounds **6-16**.

Earlier [7] we showed that values of  $W$  parameters mainly depend on the presence or absence of functional groups in the molecule structure. The presence of electron-attractive substituents shifts the  $W$  parameter toward a low field and *vice versa*. Comparing the experimental values of basic spectral parameters  $\delta_{CH_3}^{H,N}$  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 according 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<sub>2</sub> in **13**) cause the methyl group absorption in a higher field and electron-accepting nitrogroup – in a lower field compared with unsubstituted sec-butylbenzene **7**. The maximal difference between values of basic spectral parameters is 0.033 ppm ( $\delta_{CH_3}^{H,N,14} = 0.833$  ppm against  $\delta_{CH_3}^{H,N,13} = 0.800$  ppm). Therefore it is necessary to take into account the influence of substituent in a 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 exchanging of the ethyl group for the aryl one. Obviously, due to the stronger electron-accepting influence of aryl group (compared with ethyl group) in alkylbenzenes **6-16** the shift of  $\delta_{CH_3}^{H,N}$  values toward the low field should take place. However we have no 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  $\delta_{CH_3}^{H,N}$  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 haloids. Regardless of the type of haloid atom and structure of alkyl radical in haloid alkyl, the values of all founded parameters  $\delta_{Me}^H$  are within the range from 0.90 to 1.10 ppm. The values  $\delta_{Me}^H$  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 the choosing the value  $W$ , we do not take into account the less by value differences concerning the influence of substituents in the phenyl ring, as well as the presence (or absence) of methyl groups in the *n*-propyl fragment of these compounds.

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

Taking into account the above-mentioned peculiarities of the choice of virtual parameters  $W$  we extended the uncertainty interval for  $\Delta W$  by sign and value from -0.100 ppm to +0.100 ppm. In spite of the considerable negative values of differential parameters  $\Delta W^N$  for *n*-propylcontaining compounds, they found themselves in this interval. Hence, parameters  $\Delta W^N$  cannot be con-

sidered applicable to determine the absence or presence of intramolecular interaction between unbound molecule fragments in *n*-propylcontaining 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  $\Delta W^N$  are represented in the Table for sec-butylbenzenes **7**, **10** and **13–16**, **24**:  $\Delta W^{7[10]} = -0.180$  ppm and  $\Delta W^{7[9]} = -0.180$  ppm for sec-butylbenzene **7**;  $\Delta W^{10[9]} = -0.190$  ppm for *para*-sec-butylphenol **10**, as well as  $\Delta W^{13[10]} = -0.200$  ppm for *para*-sec-butylaniline **13**;  $\Delta W^{14[9]} = -0.167$  ppm for *para*-nitro-sec-butylbenzene **14**,  $\Delta W^{15[9]} = -0.196$  ppm for *para*-sec-butylanisole **15**,  $\Delta W^{16[9]} = -0.188$  ppm for *para*-sec-butylphenol acetate **16** and  $\Delta W^{24[9]} = -0.230$  ppm for 3-phenylpentane **24**. The absolute values of differential parameters  $\Delta W$  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  $\Delta\delta_{CH_3}^{H,N}$  and virtual parameters  $\Delta W$  calculated for the protons of methyl end-group in  $-\text{CH}(\text{CH}_3)-\text{CH}_2-\underline{\text{CH}_3}$  allows to assume that the interaction between methyl end-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  $\Delta W$  for *tert*-amylbenzenes **8** and **11**. Very large negative values of  $\Delta W$  parameters are represented in the Table. They exceed 0.300 ppm:  $\Delta W^{8[9]} = -0.310$  ppm for *tert*-amylbenzene **8**; as well as  $\Delta W^{11[10]} = -0.340$  ppm and  $\Delta W^{11[9]} = -0.320$  ppm for *para*-*tert*-amylphenol **11**.

The presence of very large negative differential parameters  $\Delta\delta_{CH_3}^{H,N}$  and  $\Delta W^N$ , calculated for the protons in methyl end-group in  $-\text{C}(\text{CH}_3)_2-\text{CH}_2-\underline{\text{CH}_3}$  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 intramolecular 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<sup>1</sup> in

particular), we may point to reciprocal influence of molecule fragments which are unbound by chemical bonds between each other. The circle is enclosed.

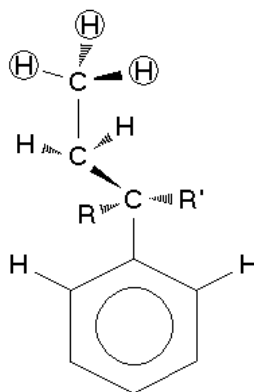


Fig. 3

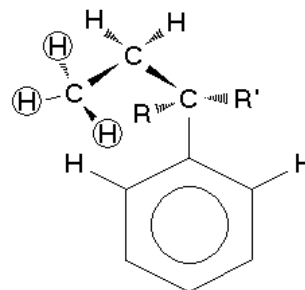


Fig. 4

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 =  $\text{CRR}^1\text{CH}_2\text{CH}_3$  and  $\text{R}^1, \text{R}^2 = \text{H}$  or  $\text{CH}_3$ ) are schematically represented in Figs. 3 and 4 respectively. Just by “partial”<sup>2</sup> influence of the system consisting of 6 annular  $\pi$ -electrons of phenyl ring on the distant methyl group of *tert*-amyl fragment (hydrogen atoms of which are inside the circles) we explain the unique by value shift of its protons toward the high yield (till value  $\delta_{CH_3}^H < 0.70$  ppm).

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-butylbenzenes – *para*-substituted cumenes (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:  $\Delta\delta_o^H = -0.021$  ppm;  $\Delta\delta_1^C = -1.56$  ppm;  $\Delta\delta_2^C = +0.61$  ppm).

<sup>2</sup> For “complete” influence of annular  $\pi$ -electrons of phenyl ring on nearby protons got under its influence the shift toward the high field is typical. Its value achieves -10 ppm.

<sup>1</sup> The spectral changes in specially fitted pairs of compounds indicate such an interaction. For instance, the difference between chemical shifts of the analogous atoms

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 some interaction in “bent” conformation for them (Fig. 4,  $R^1=R^2=H$ ).

## 4. Conclusions

The data of NMR  $^1H$  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 the 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.

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## ВЗАЄМОДІЯ НЕЗВ'ЯЗАНИХ ХІМІЧНИМИ ЗВ'ЯЗКАМИ ФРАГМЕНТІВ МОЛЕКУЛИ ЧЕРЕЗ ПРОСТІР ПІД ЧАС РЕЄСТРАЦІЇ ЯМР $^1H$ СПЕКТРІВ

**Анотація.** Проаналізовано хімічні зсуви пара-заміщених пропілбензолів загальної формули  $p-X-C_6H_4-CRR^1CH_2CH_3$  (де  $R, R^1 = H, CH_3$ ) в ЯМР  $^1H$  спектрах. За допомогою базового спектрального параметру – величини хімічного зсуву метильного протону порівняно з величиною відповідного алкану показаний вплив наявності чи відсутності арильного фрагменту на кінцеві метильні групи. Розроблено спеціальні критерії для ідентифікації і оцінювання такого ефекту. Зроблено загальний висновок, що вирогідність взаємної внутрішньомолекулярної взаємодії між незв'язаними фрагментами в молекулі трет-амілбензолу і трет-амілфенолу ( $R = R^1 = CH_3$ ) є дуже високою.

**Ключові слова:** ЯМР  $^1H$  спектр, пара-заміщений пропілбензол, спектральний параметр, диференційний параметр, віртуальний, внутрішньомолекулярна взаємодія.