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The influence of the methyl group on the chemical shifts values of all protons in mono-methylalkane molecules in the ^{1}H NMR spectra.

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Abstract. The protons chemical shifts values in the PMR spectra of methylalkanes of general formula **Nn** (when **n** is the letter designation of linear alkane, and **N** is the carbon atom number which is attached to the methyl group in the alkyl chain of **n**) have analyzed. It is calculated and discussed the individual (***N-n-i***), the arithmetic means (***N-n-i***) "standard" differential parameters (the difference between absorption of studied proton in **Nn** and its absorption in the **n**) and the "integral spectral changes" **Σ *N-n-i*** that occur in process **n → Nn**).

Keywords: chemical shift, base spectral parameters, "standard" and additional differential parameters, linear alkanes, methylalkanes, integral spectral changes, mono- and polycarbonic fragments of alkane molecule.

1. Introduction.

1.1. General comments.

In a previous report [1], we describe the results of the systematic investigations concerning the dependence between spectral parameters of the simplest aliphatic compounds – linear aliphatic molecules, containing functional end-group **Y** and it structure. The next step is planned to study the effect of the introduction of one, two or three methyl groups in the alkyl chain of the linear alkanes on NMR spectral parameters of resulted methylalkanes molecules.

In this paper we study the chemical shift values [i.e., the **base spectral parameters (*BSP*)**] of all protons that make up the "outer contour" in **"monomethyl" linear alkane molecule**. The observed "spectral changes" one can considered as the results of the introduction of one ***substituent – the methyl groups*** - in linear alkane molecule to form methylalkanes. On the other hand, the introduction of the methyl substituent in the alkyl chain is its branching process.

For a discussion of the results is very convenient and useful to be speculative selection of individual fragments of the molecule in the initial linear alkanes and in final monomethylalkanes. These fragments of the number of carbon atoms in them called as monocabonic, dicarbonic, tricarbonic and tetracarbonic fragments of alkane molecule. It is known that in the initial linear (unbranched) alkanes there are only two types of monocarbonic fragments. This is the "end" methyl groups and the "mid" methylene groups. When we introduce the "methyl substituent" instead of one of the hydrogen atoms of the terminal (end) methyl group the branch does not occur, but elongation of the carbon chain of the molecule by a single carbon atom. In the spectral parameters of newly obtained molecule essentially no change as compared with the original linear alkane molecule, since it is still only two abovementioned types of monocarbonic fragments.

Another result is the introduction of a methyl group as the substituent in the initial linear alkane molecule instead of one of the methylene group two hydrogen atoms. At new already branched "methylsubstituted" molecule, **two new types of monocarbonic fragments** are present. These are: a) the "mid" methyl group, which has been newly introduced in place of the hydrogen atoms of the methylene group, and b) the so called "methine fragment". The last was formed from the former monocarbonic methylene fragment, at which was realized replacing a hydrogen atom on the methyl group. Its carbon atom is bonded to only one hydrogen atom (i.e., the second, "remaining unsubstituted " of the original two hydrogen methylene hydrogen atoms) and three another carbon atoms. Therefore, the carbon atom in the "methine fragment" from the secondary to the tertiary turns. Both new abovementioned monocarbonic

fragments in methylalkanes are formed a new "dicarbonic fragment": **–CH(CH₃)-**. It is bounded to two parts of whole alkyl chain: $CH_3(CH_2)_k$- and $CH_3(CH_2)_l$- that existed in the linear alkane before the "methyl substitution process" occurred. In general, both these chains [$CH_3(CH_2)_k$- and $CH_3(CH_2)_l$-] have <u>different lengths</u> (k ≠ l, usually, k < l). So they called as a "shortchain" and a "longchain" methylalkane molecule fragments. If the carbon chains in both fragments of the same length (k = l), the molecule is symmetrical one and the term "short-" and "longchain" fragments meaningless.

The alkyl chain length in linear alkanes (and methylalkanes too) we are generally designated by the Latin bold letter «**n**». Thus, at the linear alkane with monocarbonic chain (methane) designated as «**a**» (i.e., "**n**" = "**a**"). The symbol "**n** = **b**" - denotes a diatomic chain in ethane. **The symbol "c" denotes propane, «d»- butane, «e»- pentane, «f»- hexane, «g» - heptane, «j» - nonane and** <u>**«k» - dodecane**</u>.

The number of each carbon atom in the alkyl chain of the linear alkane molecule **n** (and methylalkanes too) is designated by **<u>numerical symbol</u>** «**i**». <u>The same numbers «**i**», which marked the every carbon atoms in methylalkane chain are assigned to each atom of hydrogen attached to this **i**-carbon atom.</u> The **newly introduced methyl group** is indicated by the number "**N**". This numeric indicates the position of methyl groups in the alkyl chain (the number **i** of carbon atom is attached to the "newly introduced" methyl group, i.e., **i = N**). Depending on the location of the new methyl group in the carbon chain of linear alkane the formed methylalkanes present oneself the different isomers, i.e. methylalkanes of different types. So the symbol "**N**" **specified the family of methylalkanes**. For example, the introduction of "methyl substituent" to a carbon atom C-3 (**i = N = 3**) form 3-methylalkane. This type of methylalkanes denoted «**N = 3**", and the entire family of 3-methylalkanes denoted as «**3n**». Similarly, the symbols «**3n**», «**4n**» and «**5n**» marked methylalkanes families containing "a methyl substituent" respectively at C-3, C-4 and C-5. Generally all classes of monomethylalkanes one can named as "**Nn**".

The **newly introduced methyl group** is indicated by the <u>number «i»</u> to the carbon atom in the chain to which it is introduced, **with the addition of a stroke**. For example, the abovementioned 3-methylheptane is referred to as «**3g**», number of the newly introduced methyl group is «**i = 3'**»: i.e.,- $C^{3'}H^{3'}_3$, and **each of the three hydrogen atoms of this group is designated as H-3'** . Accordingly, the proton chemical shift of this methyl groups designated as «$\delta^{H,3g}_{3'}$».

Below is the numbering of the carbon and hydrogen atoms in all four families considered «**Nn**» methylalkanes.

Compounds of family «**2n**»: $C^1H^1_3-C^2H^2(C^{2'}H^{2'}_3)-C^3H^3_2-...-C^{\omega-1}H^{\omega-1}_2-C^{\omega}H^{\omega}_3$

Compounds of family «**3n**»: $C^1H^1_3-C^2H^2_2-C^3H^3(C^{3'}H^{3'}_3)-C^4H^4_2-...-C^{\omega}H^{\omega}_3$

Compounds of family «**4n**»: $C^1H^1_3-C^2H^2_2-C^3H^3_2-C^4H^4(C^{4'}H^{4'}_3)-C^5H^5_2-...-C^{\omega}H^{\omega}_3$

Compounds of family «**5n**»: $C^1H^1_3-C^2H^2_2-C^3H^3_2-C^4H^4_2-C^5H^5(C^{5'}H^{5'}_3)-C^6H^6_2-...-C^{\omega}H^{\omega}_3$

In general, <u>the monomethyl-substituted linear alkanes can exist beginning only from propane</u>, hence the most "short-chain substance" of the most "short-chain family" - «**2n**» - is the isobutane (i.e., 2-methylpropane **2c**), which contains tricarbonic alkyl chain. Accordingly, at the family «**3n**» the most "short-chain" member is a compound 3-methylpentane **3e**, which contains pentarbonic alkyl chain; in the family «**4n**» - 4- methylheptane (**4g**, heptarbonic alkyl chain), and in the family «**5n**» - 5-methylnonane (**5j**, nonarbonic alkyl chain). Note that all these compounds are symmetrical along the length of both the carbon chains [$CH_3(CH_2)_k$- and $CH_3(CH_2)_l$-; (k = l)] of the molecule. For the longchain methylalkanes, which contain a "methyl substituent" at the C-6 (**N** = 6) and further, in our sources of information lacks the necessary spectral data, and these compounds are not considered.

All methylalkanes molecules contains only <u>three different types of methyl groups</u>: the newly appeared **"mid"**, and two different types of previously existing "end" methyl groups: the so called "near end" and "far end" methyl groups.

Signal of proton in PMR spectra of methylalkanes **Nn** molecule in general designated as «$\delta^{H,Nn}_i$». In superscript part we consistently separated by a comma, specify: a) the type of the spectrum (H - proton spectrum), b) the number of substance - **Nn**; c) sometimes in brackets is number of the source of information. In the subscript part of notation we specify: the number «**i**» of the proton (or rather, its position in a specific "monocarbonic fragment" «**i**» in the alkyl chain). In every methylene groups each of two protons <u>may be (or may not be!)</u> **magnetically equivalent**. In the case of magnetic non-equivalence the upfield ("highfield") proton is designated by the letter "A", and its signal as $\delta^{H,Nn}_{iA}$ and downfield ("lowfield") – by the letter "B" ($\delta^{H,Nn}_{iB}$). For example, "far end" α-methylene protons H-6A and H-6B in 5-methyloctane **5h** denoted as $\delta^{H,5h}_{6A}$ ("upfield" proton), and "lowfield" as $\delta^{H,5h}_{6B}$. The absorption of

magnetically equivalent protons (for example, $\delta^{H,5g}{}_3$), or *"integral" absorption of two magnetically nonequivalent protons* (for example, $\delta^{H,5g}{}_4$, see below) is denoted <u>without the use of the signs " A" and "B".</u>

The discussion of spectral parameters for each of *i*-type proton of all methylalkanes of all four families **Nn** carried out by the following general scheme. Initially we discuss all methyl-substituted alkanes of **2n** family, then compounds of families "**3n**", then of families "**4n**" and, finally, "**5n**.

The first discusses the chemical shifts of the methyl groups three protons signal: a) "near end", b) "far end" c) "newly introduced" - "the mid". After this we discuss the chemical shifts of newly formed methine proton. Finally we consider the chemical shifts of two "methylene" protons in some methylene groups of the molecule. The first we examine the chemical shifts of two protons of "near end" α-methylene groups, then the chemical shifts of two protons of "far end" α-methylene group. Then, in the same sequence are considered protons of the β-methylene groups.

2. Experimental part.

We used the spectral data (chemical shifts of protons in the ^{1}H NMR spectra) taken from the literature. The choice of literature sources was grounded on the observation of their reliability and compatibility. We used only chemical shift values obtained in deuteriochloroform as a solvent and presented in the reference book [2, 3]. Spectra obtained in other solvent, e.g. CCl4, we do not examine here. The chemical shift parameters given in [2] (which are usually given up to 0.001 ppm) were obtained using instruments with different frequency: low-frequency (90 MHz) and high-frequency (300 or 400 MHz). "Low-frequency" parameters were used only in the absence of "high-frequency" value. The authors of data represented in [2] give their own attribution of spectra signals to the absorption of definite types of hydrogen atom nuclei. The authors of data represented in [3] (which are usually given up to 0.01 ppm) do not give their own attribution of spectra signals; therefore we do this by ourselves. All signals of each of the ^{1}H NMR spectra of every of methylalkanes **Nn** are arranged in a fairly narrow (less 1 ppm) range values δ^H: from 0.75 ppm to 1.70 ppm. The most of easily interpreted are triplet signals of both methyl end groups and the doublet signals of the mid methyl groups. The assignment of the multiplet signals of methylene and methine protons is often difficult, because usually in the range of magnitudes 1.0 ÷ 1.4 ppm these signals overlap, especially at long chain methylalkanes.[1]*

The "literary" values of aliphatic protons absorption of methylalkanes of **2n**, **3n, 4n and 5n** families, denoted above as "$\delta^{H,Nn}{}_i$", are shown in tables 1-4 situated at the beginning of some sections. These values are called by us the **basic spectral parameters** (shortly, **BSP**) of protons absorption. If the **BSP** value ($\delta^{H,Nn}{}_i$) is used in both sources [2 and 3] , both figures given in the table .

Every cell of the every Table has two values of **BSP** given as a fraction: numerator (without parentheses) is a value, taken from [3], and denominator (with parentheses) is the same parameter but taken from [2]. When the source [2] instead of discrete values of "*i*-type" protons signals give a numeric range, in the Table is a dash "(-)" and the footnote number, which identifies the boundaries of the interval. The same symbol "(-)" (without the footnote) we use in numerator where it is difficult to us to assign discrete value to proton absorption in data represented in [3] for substance **Nn**. In some cases (for example, in Table 1), along with authors [2] assignment of spectra signal shown in [2], we present our own assignment of these signals. In this case, a separate line (under a line that describes the author's assignment) of the corresponding numerals from our assignment are given in square brackets in bold.

The calculated values of <u>**differential spectral parameters**</u> (shortly «**DSP**»), referred to as $\Delta\delta^{H,Nn}{}_i$, along with the **BSP** values used for the convenience in discussing of the results. About **DSP** values in detail we shall say below. **DSP** values are **always given with the "+" or "-" sign**, they should be expressed in **billionths parts** (shortly, **mlrd.**), calculated from the equation: **1 ppm = 1000 mlrd.** When calculating the values of **DSP** all **BSP** values of compounds **2n − 5n**, taken from [2 and 3], are rounded to the nearest number divisible by 0.005 ppm. We estimate the inaccuracy of measurements as ± 0.02 ppm (20 **mlrd.**, see below).

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[1] *In some cases, we could not reliably attribute some signals in spectra available of [3] to absorption of the specific methylene (or methine) protons. Therefore, the basis of our research is the signal assignment in the spectra given in [2] and performed by the authors [2]. The correctness of the findings made by us in this study largely depends on the correctness of these assignments. Validation of our own attribution of spectra signals represented in [3] we see in the consistency of the data given in Tables 1-4.*

3. Discussion of results.

As mentioned above, the chemical shift of the studied proton (i.e., its **BSP** values) in the common designation system referred to as "$\delta^{H,Nn}_i$" with using an superscript and subscript symbols. The superscript part of the «**Nn**» represents the number of compound, and the subscript part of «**i**» denotes the type of the studied proton (see above).

For convenience to simplify the designation due to the failure of an superscript and subscript symbols, in this report ***we introduce a new system of designation*** for each parameter $\delta^{H,Nn}_i$. In each case the new introduced designation is duplicated the old one (i.e., with using of common superscript and subscript symbols such as "$\delta^{H,Nn}_i$"). The **BSP** values ("$\delta^{H,Nn}_i$") in the text and Tables. 1 – 4 are marked with italic black bold font as "***Nn-B-i***". The symbol "***B***" indicates that this parameter is **basic** parameter (**BSP**), and it introduced in order to distinguish the basic parameter from similar abbreviations for the differential spectral parameters (**DSP**). In the above example of the 3-methylheptane **3h** the symbol «***3-h-B-3'***» ($\delta^{H,3h}_{3'}$) denotes the magnitude of the chemical shift of the methyl protons **H-3'** of "near end" newly introduced mid methyl group $-C^{3'}H^{3'}_3$. For all or most of the compounds of each the four families dimethylalkanes **Nn** we calculated the arithmetic mean value [1] of the discussed parameter referred to as by ***underlined*** symbol «***Nn-B-i***».

The difference between the chemical shift of the every ***i***-th proton in discussed methylalkanes **Nn** and the same ***i***-th type of protons in the "standard compound", which we denote as (***etal***), we designate as the **differential spectral parameter** «$\Delta\delta^{H,Nn}_i$» (abbreviated **DSP**). Depending on tasks it may be selected the ***different reference compounds***. The **DSP** parameters of all of the discussed methylalkanes **Nn** are calculated for each of the ***i***- type proton as follows: $\Delta\delta^{H,Nn}_i = \delta^{H,Nn}_i - \delta^{H,etal}_i$, and in our proposed system of notation as : ***N-n-D-i*** = ***N-n-B-i - etal-B-i***.

It is known that in every linear alkanes are present only two types of "monocarbonic fragment". There are the "end methyl group" and "mid methylene group". For protons of these groups we determine previously [1] the average values of **BSP**. There are (rounded to the nearest number divisible by 0.005 ppm), respectively, ***0.880*** ppm and ***1.270*** ppm. Therefore, as **"standard compound"** for comparison of the reference parameter **BSP** of "threeprotonic" signal of each of the methyl groups in the investigated methylalkanes **Nn** we shall use the **"standard reference parameter"** - an averaged **BSP** value of "end methyl groups" protons in the long-chain linear alkane (designated as «$\delta^H_{end.}$»). We denote this parameter as ***etal-CH₃*** **= 0.880** ppm. For comparison of methylene and methine protons we use as a **"standard reference parameter"** (by analogy with the methyl groups) an average **BSP** value of "mid methylene groups" protons in long-chain linear alkanes «$\delta^H_{mid.}$». We denote it as ***etal-CH₂*** **= 1.270** ppm.

These type of **DSP** we named as **'standard'** and denote a shorter red bold italic symbol: (***DSP=Nn-i*** instead of «***N-n-D-i***»), wherein no letter «D». The **"standard"** differential parameters of of **methyl group protons** is calculated as follows ***Nn-i = N-n-B-i − 0.880*** ppm (or: $\Delta\delta^{H,Nn}_i = \delta^{H,Nn}_i - \delta^H_{end.} = \delta^{H,Nn}_i − 0.880$ ppm). If the compared signal ***N-n-B-i*** ($\delta^{H,Nn}_i$) is located in a ***stronger field than the standard signal*** ($\delta^H_{end.}$ **= 0.880 ppm**), the parameter ***Nn-i has the sign "minus" and vice versa***. Similarly, the **"standard"** differential parameters of methylene and methine protons is calculated as follows: ***Nn-i = N-n-B-i − 1.270*** ppm (or $\Delta\delta^{H,Nn}_i = \delta^{H,Nn}_i − 1.270$ **ppm**) and has the same signs. The values of "**standard**" differential parameters ***DSP=Nn-i*** expressed in ***billionths parts*** (**mlrd.**), i.e. $\Delta\delta^H \times 1000$. In addition to the **"standard"** ***DSP=Nn-i*** sometimes may be used other the **"additional"** type of **DSP**, but in this work there is no need in this.

The **measurement error** of **BSP** values is adopted by us equal to **20 mlrd.** So the **BSP** values of methyl groups fall into the "strip" values equal to ***etal-CH₃*** **= 0.880 ppm ± 0.020 ppm** (i.e., in the range from 0.860 ppm to 0.900 ppm) and values of methylene (and methine) groups **BSP** values fall into the "strip" values ***etal-CH₂*** **= 1.270 ppm ± 0.020 ppm** (i.e., in the range from 1.250 ppm to 1.290 ppm). So the abovementioned "strip" **BSP** values should be considered as "insufficiently valid"**²***. Hence the differential parameters of **DSP**, which are in absolute value less than or equal to 20 mlrd., either not at all be discussed, or in the discussion will be considered as " insufficiently   valid".

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²* *Choice of bandwidth is an author's subjective decision. It depends on the intuition of the author and his understanding of the nature of the material being studied. Perhaps the width of the "interval of uncertainty" equal to **40 mlrd.**, is too high, and it could be estimated as **20 mlrd.** However, in this case, we prefer to "safe" in order to consider only really (not imaginary) existing spectral effects.*

3. 1. The Families of 2-methylalkanes <u>2n.</u>

Table 1 shows the proton **BSP** values of seven compounds of the 2-methylalkanes **2n** family: 2-methylbutane **2d**, 2-methylpentane **2e**, 2-methylhexane **2f**, 2-methylheptane **2g**, 2-methyloktane **2h**, 2-methylnonane **2j** and 2-methyldodecane **2k**. For the first four substances the spectral data taken from both sources are in good agreement with each other; for the other three compounds - only the data of [2]. Altogether Table 1 shows the 11 sets of parameters. The spectral data of the most "short chain" 2-methylalkane **2n**: the gaseous 2-methylpropane (isobutane) **2c** are absent in both sources, so are not discussed.

Table 1

The <u>base spectral parameters</u> (**BSP**) values, i.e. $\delta^{H,2n}_i$ chemical shifts of *i*-type protons of 2-methylalkanes **2n** of the general formula $C^1H^1_3-C^2H^2(C^{2'}H^{2'}_3)-C^3H^3_2-C^4H^4_2-C^5H^5_2-...-C^{\omega-1}H^{\omega-1}_2-C^\omega H^\omega_3$

Number of compound	Formula	The **BSP** values («$\delta^{H,2n}$») in ppm of specified number of "*i*-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.							
		3H 3x[H-1] (d)	1H [H-2] (m)	3H 3x[H-2'] (d)	2H [H-3] (m)	2H [H-4] (m)	2H [H-5] (m)	2H [H-(ω-1)] (m)	3H 3x[H-ω] (t)
2d	$CH_3-CH(CH_3)-CH_2-CH_3$	0.87 (0.869)	1.45 (1.447)	0.87 (0.869)	1.20 (1.20)				0.86 (0.865)
2e	$CH_3-CH(CH_3)-(CH_2)_2-CH_3$	0.865 (0.864)	1.54 (1.541)	0.865 (0.864)	1.15 (1.15)	1.29 (1.29)			0.88 (0.880)
2f	$CH_3-CH(CH_3)-(CH_2)_3-CH_3$	0.87 (0.867)	1.52 (1.518)	0.87 (0.867)	1.17 (1.17)	1.26 (1.27)	1.26 (1.27)		0.89 (0.889)
2g	$CH_3-CH(CH_3)-(CH_2)_4-CH_3$	0.86 (0.870)	1.52 (1.524)	0.86 (0.870)	1.15 (1.16)	1.26 (1.26)	1.26 (1.26)	1.26 (1.26)	0.89 (0.889)
2h	$CH_3-CH(CH_3)-(CH_2)_5-CH_3$	(0.864)	(1.517)	(0.864)	(1.16)	(1.26)	(1.26)	(1.26)	(0.884)
2j	$CH_3-CH(CH_3)-(CH_2)_6-CH_3$	(0.870)	(1.522)	(0.870)	(1.16)	(1.27)	(1.27)	(1.27)	(0.889)
2k	$CH_3-CH(CH_3)-(CH_2)_9-CH_3$	(0.863)	(1.516)	(0.863)	(1.155)	(1.26)	(1.26)	(1.26)	(0.882)

3. 1. 1. The *BSP* values of "near end" (H-1) and mid (H-2') methyl group protons in 2-methylalkanes 2n<u>.</u>

In the 2-methylalkanes **2n** family the "near end" methyl groups ($C^1H^1_3$) and mid methyl groups ($C^{2'}H^{2'}_3$) are connected to one and the same carbon atom C-2 and so do not differ each other. Therefore, both types of these methyl groups are **magnetically equivalent** and are discussed together in this section. Hence, the base (**BSP**) values, as well as standard differential (**DSP**) values of their parameters are the same, i.e. **2n-B-1 = 2n-B-2'** or ($\delta^{H,2n}_1 = \delta^{H,2n}_{2'}$) and **2n-1 = 2n-2'** (or $\Delta\delta^{H,2n}_1 = \Delta\delta^{H,2n}_{2'}$). Let's designate the **hexaprotonic doublet signal of "near end" methyl groups ($C^1H^1_3$) and mid methyl groups ($C^{2'}H^{2'}_3$)** in each of the 2-methylalkanes **2n** <u>exclusively as only protons H-1</u>, namely : **2n-B-1** ($\delta^{H,Nn}_1$) to (**BSP**) and **2n-1** ($\Delta\delta^{H,Nn}_1$) to **DSP** .

All eleven **<u>2n-B-1</u>** values in Table 1, are found in a narrow range of 0.860 to 0.870 ppm, which is near the value of the "standard" reference parameter **etal-CH₃ = 0.880** ppm. The closeness of each of the **<u>2n-B-1</u>** parameters with each other and the value **etal-CH₃ = 0.880** ppm means that all 11 differential parameters **2n-1** will be <u>very small in magnitude and negative in sign.</u>

During the results discussion it is often advisable to operate not the individual parameters values of each compound of the **Nn** family, but discussed the **parameter mean value** calculated for the individual parameters of these families of compounds (or part thereof). And the arithmetic mean value of the base parameter **BSP**, and the "standard" differential parameters **DSP** (in abbreviated form, "the arithmetic mean parameter") are denote by <u>underlining the first term of symbol</u> (see below).

Just in the case of a large number of almost equal base parameters **2n-B-1** it seems appropriate to calculate and discuss the parameters **<u>2n-B-1</u>** and **<u>2n-1</u>** arithmetic mean values. The base arithmetic mean parameter **<u>2n-B-1</u>** (denoted using superscript and subscript symbols as "$\delta^{H,aver.2n}_{1+2'}$") is calculated from the 11 sets of **BSP** values given in Table 1 and is equal to **0.867 ppm**. Hence the arithmetic mean differential

parameter $2n$-1 (denoted using superscript and subscript characters as "$\Delta\delta^{H,aver.2n}_{1+2}$") is ≈ **-13 mlrd.**
When this value is rounded to the nearest number divisible by 0.005 ppm (or **5 mlrd.**), we get a value: $2n$-1
= **-15 mlrd.** The absolute value of this numeric is significantly less of the strip of "insufficiently validity" of
the spectral parameters (20 **mlrd.**). Therefore the value of the "rounded" the arithmetic mean parameter:
$2n$-1 = **-15 mlrd.** is not enough to be considerably valid and so not subject to further discussion.

3. 1. 2. The *BSP* values of "far end" (H-ω) methyl group protons in 2-methylalkanes 2n.

The "far end" methyl groups in methylalkanes **Nn** structure (including the 2-methylalkanes **2n** family)
designated as "$C^{\omega}H^{\omega}_3$". Using the symbol «ω» caused the fact, the specific number «*i*» of the terminal
carbon and hydrogen atoms depends of the length of the alkyl chain in molecule. Table 1 shows the 11
values of *BSP* triprotonic triplet signal *2n-B-ω* of all seven compounds of **2n** family. All of these values are
at rather broad range from 0.860 to 0.890 ppm.

In most longchain ("true longchain") 2-methylalkanes **2n** (for example, **2j** and **2k**) the branching at
the carbon atom C-2 is located far enough (at 6 and 9 carbon atoms in the chain, respectively) of the "far
end" methyl group $C^{\omega}H^{\omega}_3$. It is expected that branching at C-2 virtually no impact on the *BSP* values of
three protons H-ω, and parameters *2n-B-ω* in these longchain 2-methylalkanes **2n** within measurement
error will be approximately equal the magnitude *etal-CH₃* = **0.880** ppm. At the same time, for the most
shortchain 2-methylbutane **2d**, it is likely that on the value of *2n-B-ω* = *2d-B-4* = 0.86 (0.865 ppm) will
affect the proximity of branching at C-2, which is separated from the "far end" methyl group $C^{\omega}H^{\omega}_3$ (in this
case $C^4H^4_3$) just by one carbon atom chain ($C^3H^3_2$).

Indeed, the value *2n-B-ω* = *2d-B-4* = 0.86 (0.865 ppm) is quite significantly different from the
values of other parameters *2n-B-ω* (0.88 - 0.89 ppm), so it seems appropriate to consider it separately
from them. For "true longchain" 2-methylalkanes **2n** (starting with 2-methylpentane **2e**) the arithmetic
mean parameters *2n-B-ω* = 0.886 ppm (and so *2n-ω* = **+6 mlrd.**) were calculated from the 9 values of *2n-B-ω* parameter.

For the shortchain 2-methylbutane **2d** the individual "standard" differential parameter *2d-4* has a
small negative value and is equal to, either *2d-1* = **-15 mlrd.** [3], or *2d-1* = **-10 mlrd.** [2], and the parameter
2e-5 for supposable midchain 2-methylpentane **2e** is already **zero** (*2e-1* = **0 mlrd.**). For the rest of the
"true" longchain 2-methylalkanes **2n**, starting from 2-methylhexane **2f**, the every individual parameter *2n-ω* has relatively **small positive value** (from +2 to +10 **mlrd.**), which is not coming out, however, for the
accepted limit (20 **mlrd.**). The arithmetic mean parameter *2n-ω* value, calculated with 7 *BSP* values of
compounds **2f** - **2k**, is ≈ +7 **mlrd.** When this value is rounded to the nearest number divisible by 0.005 ppm
(or **5 mlrd.**), we get a value: *2n-ω* = **+5 mlrd.** The absolute value of this arithmetic mean parameter is much
less of the accepted limit of 20 **mlrd.**, so the parameter *2n-ω* = **+5 mlrd.** not subject to further discussion.

Obviously, as the chain elongation the individual values of *2n-ω* parameters are <u>gradually increased</u>
from a **negative** (in the shortchain 2-methylbutane **2d**) **through zero** (midchain 2-methylpentane **2e**) to
positive value in the "true longchain" 2-methylalkanes **2n** (**2f** - **2k**). According to this criterion, 2-methyl
pentane **2e** can be considered as "midchain" 2-methylalkane, i.e., intermediate between shortchain 2-
methylbutane **2d** and longchain 2-methylalkanes **2n**, which begin with a 2-methylhexane **2f**.

3. 1. 3. The *BSP* values of methine protons (H-2) in 2-methylalkanes 2n.

The methine protons "C^2H^2" in the structure of 2-methylalkanes **2n** are designated as H-2. Table 1
shows the 11 *BSP* values of multiplet signal *2n-B-2* in the PMR spectra of seven compounds of the family
2n. All these values are in the range of 1.45 to 1.54 ppm.

As in the case of "far end" methyl groups the seven 2-methylalkanes **2n** can be divided into three
parts: a) one "shortchain" (2-methylbutane **2d**); b) one "midchain" 2-methylpentane **2e**, the five
"longchain" compounds (starting from 2-methylhexane **2f**). For "shortchain" 2-methylbutane **2d**, the *BSP*
values *2d-B-2* is equal to 1.45 ppm (1.447 ppm). For "midchain" 2-methylpentane **2e** the *BSP* values *2e-B-2* is equal to 1.54 ppm (1.541 ppm). For the remaining five "longchain" compounds (**2f** - **2k**) the 7 individual
BSP values *2n-B-2* have an intermediate position and are in a very narrow value range: 1.51 ÷ 1.52 ppm,
so *2n-B-2* = **1.515** ppm.

Accordingly, the differential **DSP** parameters **2n-2** are different for all three groups of compounds **2n**. Individual parameter of the "shortchain" 2-methylbutane **2d** is equal: **2d-2** = 1450 - 1270 = **+180 mlrd.** For ""midchain" 2-methylpentane **2e** the **DSP** values **2e-2** is much larger and is equal: **2d-e** = **+270 mlrd.** The arithmetic mean value of the parameter **2n-2** in longchain 2-methylalkanes (**2f** - **2k**) is equal to: **2n-2** = **+245 mlrd.** The methine proton H-2 absorption at all 2-methylalkanes **2n** is significantly (180 – 270 **mlrd.**) **shifted downfield** compared to the reference parameter **etal-CH$_2$ = 1.270 ppm**.

3. 1. 4. The *BSP* values of methylene protons in 2-methylalkanes 2n.

The structure of all 7 compounds of the 2-methylalkanes **2n** family (except isobutane **2c**, the PMR spectrum of which we do not consider) contains some methylene protons. They enter in all monocarbonic fragments beginning from $C^3H^3_2$ (α-protons) to the methylene fragment $C^{\omega-1}H^{\omega-1}_2$.

3. 1. 4. 1. The *BSP* values of α-methylene protons (H-3) in 2-methylalkanes 2n.

The α-methylene group in the structure of 2-methylalkanes **2n** is designated as "$C^3H^3_2$". Both protons H-3 in it are considered as **_magnetically equivalent_**, i.e. given one (although multiplet) signal. Table 1 shows the 11 **BSP** values of multiplet signal **2n-B-3** of two protons H-3 in the PMR spectra of seven compounds of the family **2n**. All these values are within a rather narrow range from 1.15 to 1.20 ppm.

As in previous cases, the seven 2-methylalkanes **2n** can be divided into three parts: a) one shortchain (2-methylbutane **2d**); b) one midchain 2-methylpentane **2e**, the five longchain compounds (starting from 2-methylhexane **2f**). For shortchain 2-methylbutane **2d**, the **BSP** values **2d-B-3** is equal to 1.20 ppm (1.20 ppm). For midchain 2-methylpentane **2e** the **BSP** values **2e-B-3** is equal to 1.15 ppm (1.15 ppm). For the remaining five longchain compounds (**2f** - **2k**) the 7 individual **BSP** values **2n-B-3** have an intermediate position and are in a very narrow value range: 1.15 ÷ 1.17 ppm, so **2n-B-3 = 1.160** ppm.

We believe that all 7 compounds of the 2-methylalkanes **2n** family according the parameter **2n-B-3** it is correct to divide into two (not three) groups. The first is only a shortchain 2-methylbutane **2d**, and the second - the remaining 6 compounds **2e-2k**.

The individual differential parameters **2n-3** are calculated for all seven 2-methylalkanes **2n**: **2d-3** = 1200 − 1270 = **-70 mlrd.**; **2n-3** = **-110 mlrd.** The absorption of α-methylene protons H-3 in all 2-methylalkanes **2n** is considerably **shift upfield** compared to the reference parameter **etal-CH$_2$ = 1.270 ppm**.

3. 1. 4. 2. The *BSP* values of β-methylene protons (H-4) in 2-methylalkanes 2n.

The β-methylene group in the structure of 2-methylalkanes **2n** is designated as "$C^4H^4_2$". It is absent in the "most shortchain" 2-methylbutane **2d**. Therefore, when we consider the β-methylene protons H-4, the term of "most shortchain" 2-methylalkane **2n** goes to the former "midchain" 2-methylpentane **2e**.

Both protons H-4 in it are considered as magnetically equivalent, i.e. given one (although multiplet) signal. Table 1 shows the 9 **BSP** values of multiplet signal **2n-B-4** of two protons H-4 in the PMR spectra of six compounds of the family **2n**. All these values are within a rather narrow range from 1.26 to 1.29 ppm.

As in previous cases, the six 2-methylalkanes **2n** can be divided into two parts: a) one "shortchain" (2-methylpentane **2e**); b) the five "longchain" compounds (starting from 2-methylhexane **2f**). For the "shortchain" 2-methylpentane **2e** the **BSP** values **2e-B-4** is equal to 1.29 ppm (1.29 ppm). For the remaining five "longchain" compounds (**2f** - **2k**) the 7 individual **BSP** values **2n-B-4** are in a narrow value range: 1.26 ÷ 1.27 ppm, directly about a standard parameter **etal-CH$_2$ = 1.270 ppm**.

The arithmetic mean value of the parameter **2n-4** in longchain 2-methylalkanes (**2f** - **2k**) is equal to: **2n-4** = **-10 mlrd.** The β-methylene protons H-4 absorption at all 2-methylalkanes **2n** is practically coincides with the reference parameter **etal-CH$_2$ = 1.270 ppm**.

The value of the individual differential parameter **2e-4** = 1290 − 1270 = **+20 mlrd.**, and the arithmetic mean value of the parameter **2n-4** in longchain 2-methylalkanes (**2f** - **2k**) is equal: **2n-4** = **-10 mlrd.** The β-methylene protons H-4 absorption at all 2-methylalkanes **2n** is **practically coincides** with the reference parameter **etal-CH$_2$ = 1.270 ppm**.

3. 2. The Families of 3-methylalkanes 3n.

Table 2 shows the proton **BSP** values of six compounds of the 3-methylalkanes **3n** family: the "reverse numbered" 3-methylbutane **3d** (see below), 3-methylpentane **3e**, 3-methylhexane **3f**, 3-methylheptane **3g**, 3-methyloktane **3h** and 3-methylnonane **3j**. For the first four substances the spectral data taken from both sources are in good agreement with each other; for the other three compounds - only the data of [2].

The table 2 we repeatedly include the base parameter set for a 2-methylbutane **2d** (which is marked with an asterisk), taken from Table 1. The numbering of carbon atoms in the chain of this compound in Table 2 is reversed (renumbered back), whereby it can be regarded as "3-methylbutane **3d**", which in this case is regarded as the "most shortchain" of all 3-methylalkanes **3n**. As a result, the reverse renumbering of second alkyl chain [$CH_3(CH_2)_l$-, see above, which consisting of just one carbon atom C -4)], in reality is shorter than the first chain [$CH_3(CH_2)_k$-, see above], beginning with the C-1 (instead be longer). Therefore, the "3-methylbutane" **3d** we call the "wrong" 3-methylalkane **3n** (as the right of his name should be 2-methyl butane **2d**!). However, we consider it appropriate to discuss its spectral parameters together with the data the other "right" 3 methylalkanes **3n**. This practice will be continued and further (4-methyl- **4n** and 5-methylalkanes **5n**).

As a result of inclusion in table 2 of the "reverse numbered" "3-methylbutane **3d**" there are 8 sets of parameters of six 3-methylalkanes **3n**. For the absorption of each type of protons in the spectrum of 3-methylpentane **3e** authors [2] provide the extensive numerical intervals. So we have not included these data in the discussion of the results. From the presented in [3] spectrum of 3-methylhexane **3f** we managed to include only absorption signals of methyl protons. For the remaining three 3-methylalkanes **3g - 3j** data listed in [2] are available. Let's note that 3-methylalkanes **3n** protons of some methylene groups are **magnetically equivalent.**

Table 2

The _**base spectral parameters**_ (**BSP**) values, i.e. $\delta^{H,3n}_i$ chemical shifts of _i_-type protons of 3-methylalkanes **3n** of the general formula $C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4_2\text{-} C^5H^5_2\text{-}\ldots\text{-}C^\omega H^\omega_3$

Number of compound	Formula	The **BSP** values («$\delta^{H,3n}_i$») in ppm of specified number of "_i_-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.								
		3-x [H-1] (t)	1-ro [H-2A] (m)	1-ro [H-2B] (m)	1-ro [H-3] (m)	3-x [H-3'] (d)	1-ro [H-4A] (m)	1-ro [H-4B] (m)	2-x [H-5] (m)	3-x [H-ω] (τ)
3d*	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$	0.86 (0.865)	1.20 (1.20)	1.20 (1.20)	1.45 (1.447)	0.87 (0.869)				0.87 (0.869)
3e	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$	0.860 (-)ᵃ	1.12 (-)ᵇ	1.34 (-)ᵇ	1.24 (-)ᵇ	0.845 (-)ᵃ	1.12 (-)ᵇ	1.34 (-)ᵇ		0.86 (-)ᵃ
3f	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}(CH_2)_2\text{-}CH_3$	0.86 (0.857)	(-) (1.13)	(-) (1.33)	(-) (1.33)	0.845 (0.841)	(-) (1.08)	(-) (1.28)	(-) (1.30)	0.88 (0.879)
3g	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}(CH_2)_3\text{-}CH_3$	(0.858)	(1.14)	(1.35)	(-)ᶜ	(0.845)	(1.09)	(1.23)	(-)ᶜ	(0.891)
3h	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}(CH_2)_4\text{-}CH_3$	(0.855)	(1.13)	(1.35)	(-)ᵈ	(0.842)	(1.08)	(1.23)	(-)ᵈ	(0.885)
3j	$CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}(CH_2)_5\text{-}CH_3$	(0.855)	(1.12)	(1.32)	(1.34)	(0.841)	(1.08)	(1.24)	(-)	(0.884)

a)   0.69-1.01 м.д.; b) 1.01-1.57 м.д.; c) 1.22-1.35 м.д.; d) 1.22-1.30 м.д.

3. 2. 1. The *BSP* values of methyl group protons in 3-methylalkanes 3n.

In the family of 3-methylalkanes **3n** (unlike the above-considered family of 2-methylalkanes **2n**) the "near end" methyl groups $C^1H^1_3$ is *not equivalent* to the mid methyl groups $C^{3'}H^{3'}_3$. These methyl groups are connected to different carbon atoms (C-2 and C-3 respectively). Therefore, the spectral parameters *3n-B-1* ($\delta^{H,3n}_1$) of the "near end" $C^1H^1_3$ methyl group protons (i.e., protons, H-1) are considered separately from the parameters *3n-B-3'* ($\delta^{H,3n}_{3'}$) of mid methyl group $C^{3'}H^{3'}_3$ protons (i.e., H-3').

3. 2. 1. 1. The *BSP* values of "near end" methyl group protons (H-1) in 3-methylalkanes 3n.

In the PMR spectra of 3-methylalkanes **3n** the triprotonic signal of the "near end" methyl groups ($C^1H^1_3$) (i.e., three protons H-1) appears as a distinct triplets and so is easily interpreted.

All 8 sets of values of the basic parameters **3n-B-1** (including two sets of "reversing" parameters **3d-B-1**) are located in a very narrow (**10 mlrd.**) interval in a range from 0.855 to 0.865 ppm. This interval is close to the value "standard "reference parameter ***etal-CH₃* = 0.880 ppm**. Nearness each of the values **3n-B-1** with each other and also to the "standard" parameter value means that all 8 differential parameters *3n-1* will be <u>small in magnitude and negative in sign</u>.

As mentioned above, in the "most shortchain" "reverse numbered 3-methylbutane **3d**" the second branch [CH₃(CH₂)ᵢ-, see above] consisting of just one methyl group $C^4H^4_3$. This circumstance may influence the value of the "wrong" parameter **3d-B-1**. In fact, both sets of the basic "wrong" parameter **3d-B-1** = **2d-B-4** = 0.860 (0.865 ppm) are shifted (albeit very slightly) downfield compared with all the other 6 sets of "correct" parameters **3n-B-1**. If you do not consider this "wrong" parameter **3d-B-1**, then the interval of the remaining six sets of "correct" parameters **3n-B-1** further will narrow to a size of 5 **mlrd.** (of 0.855 to 0.860 ppm). It is therefore correct to discuss the "wrong" parameter **3d-B-1** apart from the other **3n-B-1** values of more "longchain" 3-methylalkanes **3n**, for which we calculated the arithmetic mean differential parameter *3n-1*.

The rounded value of *3n-1* («$\Delta\delta^{H,ycp.3n}_1$») parameter calculated from 6 sets of values **BSP** (**-23 mlrd.**), is equal to: *3n-1* = **- 25 mlrd.**, which is slightly larger in absolute value than the "strip of insufficiently validity" of the spectral parameters (**20 mlrd.**).

3. 2. 1. 2. The *BSP* values of "far end" methyl group protons (H-ω) in 3-methylalkanes 3n.

The "far end" methyl groups in 3-methylalkanes family **3n** are designated as "$C^\omega H^\omega_3$". The triprotonic signals manifested as a distinct triplet and easy to interpret. In most longchain ("true longchain") 3-methylalkanes **3n** (for example, **3h** and **3j**) the branching at the carbon atom C-3 is located far enough of the "far end" methyl group $C^\omega H^\omega_3$. It is expected that branching at C-3 virtually no impact on the *BSP* values of three protons H-ω. Within measurement error the parameters **3n-B-ω** (as in longchain 2-methylalkanes **2n**) in these longchain 3-methylalkanes **3n** will be approximately equal the magnitude of "standard" reference parameter ***etal-CH₃* = 0.880** ppm. In formally "the most shortchain 3-methylalkane", the "reverse numbered" 3-methylbutane **3d**, the parameter **3d-B-4** consideration for the above reasons is inappropriate.

The symmetrical 3-methylpentane **3e** should be considered as shortchain alkane in respect that branching occurs relatively near "far end" methyl group (at β-carbon atom of chain). Therefore, it is considered separately. 3-methylhexane **3f**, by analogy with 2-methylalkanes **2n** may be regarded as "midchain", i.e. intermediate between the "shortchain" 3-methylpentane **3e** and "true longchain" 3-methylalkanes **3n**, which obviously start with a 3-methylheptane **3g**. For 3-methylheptane **3f** the basic parameter **3f-B-6** are 0.88 ppm and (0.879 ppm) respectively. These though very slightly, but still less than the other three parameters **3n-B-ω** (**3g-B-7** = 0.891 ppm; **3h-B-8** = 0.885 ppm and **3j-B-9** = 0.884 ppm).

However, by analogy with the methyl protons H-ω in 2-methylalkanes **2n**, let's calculate an arithmetic mean value of the differential parameter *3n-ω* (**+4 mlrd.**) using 5 data sets of four 3-methylalkanes **3n**: three longchain (**3g, 3h** and **3j**) and one midchain (**3f**). This rounded parameter, *3n-ω* = **+5 mlrd.**, is positive in sign and equal the same rounded value obtained in the calculation using only 3 parameters of three sets of "true longchain" 3-methylalkanes (**3g, 3h** and **3j**).

In shortchain **symmetrical** 3-methylpentane **3e** the proton H-1 and H-5 parameter values of "near end" ($C^1H^1_3$) and "far end" ($C^5H^5_3$) methyl groups are the same (*3e-1 = 3e-5* = **-20 mlrd.**). As mentioned above, a negative sign of this parameter may affect the proximity of branching at C-3 (only via one methylene group). It is possible that the same effect (but to a lesser degree), takes place in the midchain 3-methylhexane **3f**, where the "far end" differential parameter already has almost zero: *3f-6* = **0 mlrd.** (**-1**

mlrd.). Changing the values of "standard differential parameters" of the "far end" methyl groups protons **3n-ω** in 3-methylalkanes **3n** as chain extension reproduces almost exactly the same changes of "standard differential parameters" of the "far end" methyl groups protons **2n-ω** in 2-methylalkanes family **2n** discussed above.

3. 2. 1. 3. The *BSP* values of the newly introduced mid methyl group protons (H-3') in 3-methylalkanes 3n.

Mid methyl group in the 3-methylalkanes **3n** are designated as "$C^{3'}H^{3'}_3$", and their three protons as H-3'. In the PMR spectrum of 3-methylalkanes **3n** the signal of newly introduced mid methyl group protons (H-3') is clearly manifested in the form of a doublet, so easy to interpret. The *BSP* values of these three protons labeled as **3n-B-3'** ($\delta^{H,3n}_{3'}$).

In formally "the most shortchain of 3-methylalkanes", i.e., "reverse numbered" "3-methylbutane **3d**", the methyl group $C^{3'}H^{3'}_3$ we are interested in was previously discussed in the section 3.1.1. Its parameter (**3d-B-3'**) is designated there as a **2d-B-2'** = **2d-B-1** = 0.87 ppm. For the abovementioned reasons, this parameter does not participate in the discussion.

In this section (as in Section 3.1.1) there is no need in dividing of 3-methylalkanes **3n** to the shortchain 3-methylpentane **3e**, midchain 3-methylhexane **3f** and longchain 3-methylalkanes **3g - 3j**. All 6 sets of values of the five basic parameters **3n-B-3'** are in a very narrow range of 0.840 to 0.845 ppm. This interval is **sufficiently far upfield shifted** from a" standard" reference parameter **etal-CH₃ = 0.880 ppm**. Such a large upfield shift implies a relatively large negative differential parameters **3n-3'** value of each **3e - 3j** compounds. The arithmetic mean differential parameter **3n-3' = -37 mlrd.** calculated from the six sets of data shown in Table 2 for five 3-methylalkanes **3e - 3j**. The rounded value **3n-3' = -35 mlrd.** indicates the **most significant upfield shift of mid methyl group signal** in 3-methylalkanes **3n** family compared with signals of other above-considered methyl groups.

3. 2. 2. The *BSP* values of methine protons (H-3) in 3-methylalkanes 3n.

The methine groups in the 3-methylalkanes **3n** are designated as "C^3H^3", and their only proton as H-3. In the PMR spectrum of 3-methylalkanes **3n** the signal of methine proton manifests itself as a multiplet, often superimposed on multiplet methylene groups signals (so it is not easy to interpret). The *BSP* values of these proton labeled as **3n-B-3** ($\delta^{H,3n}_3$).

Table 2 lists the five **3n-B-3** discrete values. Two of those are discussed above, as a parameter **2d-B-2** in 2-methylbutane **2d**. They in the "reverse numbered" "3-methylbutane **3d**" will be the **3d-B-3** parameters, and more will not be discussed, since only a formally are the parameters of **3n-B-3** type. In the spectrum PMR of a symmetrical 3-methylpentane **3e** given in [2], the multiplet signal centered 1.24 ppm, we interpreted (may be insufficient reliability) as the parameter **3e-B-3**. Table 2 shows also two taken from [2] discrete parameters **3n-B-3**: **3f-B-3** = 1.33 ppm and **3j-B-3** = 1.34 ppm. Both of these values are significantly different from the our proposed value **3e-B-3** = 1.24 ppm. A possible reason for the difference, as in case of above-considered 2-methylalkanes **2n**, is a shortness of second chain in the symmetrical midchain 3-methylpentane **3e** compared with the longchain compounds **3f** and **3j**.

The rounded arithmetic mean differential value of longchain parameter **3n-3** is positive and equal to: **3n-3 = +65 mlrd.** The individual parameter **3e-3 = - 30 mlrd.** on the contrary, has a negative value.

3. 2. 3. The *BSP* values of methylene protons in 3-methylalkanes 3n.

The structure of all 6 compounds of the 3-methylalkanes **3n** family contains several different types of methylene protons. They enter in all monocarbonic fragments beginning from $C^3H^3_2$ (α-protons) to the methylene fragment $C^{\omega-1}H^{\omega-1}_2$.

The all compounds of 3-methylalkanes **3n** family structure contain several different types of methylene protons. The monocarbonic fragment $C^2H^2_2$ we name as "near end", and its protons H-2 are called as "near end", α-protons. All monocarbonic fragments beginning from $C^4H^4_2$ and ending the methylene moiety $C^{\omega-1}H^{\omega-1}_2$ (including α-protons H -4 of fragment $C^4H^4_2$) are considered as "far end". The β-protons spectral parameters of monocarbonic fragment $C^5H^5_2$ and more remote methylene groups will not be discussed due to lack of reliable spectral data.

The signals of each of the methylene protons are **complex multiplet**, and its attribution is often difficult. Particularly note, that both the proton in each of α-methylene groups are **magnetically nonequivalent**, i.e. give two different multiplet signals.

3. 2. 3. 1. The *BSP* values of "near end" α-methylene protons (H-2) in 3-methylalkanes 3n.

Two magnetically nonequivalent protons of the "near end" α-methylene group $C^2H^2_2$ are designated as H-2A and H-2B. They are attached to the carbon atom C-2 and disposed in a space between "near end" methyl group $C^1H^1_3$, and the newly formed dicarbonic fragment "$C^3H^3(C^{3'}H^{3'}_3)$".

Both H-2 protons signals ($\delta^{H,3n}_2$) are designated as *3n-B-2.* The *BSP* value of upfield (H-2A, respectively, $\delta^{H,3n}_{2A}$) and the downfield (H-2B, respectively, $\delta^{H,3n}_{2B}$) protons are labeled as *3n-B-2A* and *3n-B-2B*. The "aggregated" basic parameter of these two protons H-2 is designated as *3n-B-2*. It is numerically equal to half the sum of the chemical shifts, i.e.: *3n-B-2* = (*3n-B-2A* + *3n-B-2B*)/2. The "aggregated" (including arithmetic mean) differential parameters are calculated for all three types' protons and designated as *3n-2A, 3n-2B, <u>3n-2A, 3n-2B,</u> 3n-2, <u>3n-2.</u>*

3. 2. 3. 1. 1. The *BSP* values of upfield "near end" α-methylene protons (H-2A) in 3-methylalkanes 3n.

As before (see section 3. 2. 1. 3.), we jointly reviewed all *BSP* value of upfield H-2A protons of all 3-methylalkanes **3e - 3j** (i.e., all *3n-B-2A* parameters), including the shortchain symmetrical 3-methylpentane **3e** and midchain 3-methylhexan **3f** (but without the "wrong" "reverse numbered" "3-methylbutane **3d**"). All 5 sets of values of basic parameters *3n-B-2A* are in a narrow range from 1.120 to 1.140 ppm. <u>This interval is significantly shifted upfield on the value of the "standard" reference parameter *etal-CH₂* = 1.270 ppm</u>. Such a large upfield shift implies a **relatively large <u>negative</u>** individual differential parameters *3n-2A* value of each **3e - 3j** compounds. The rounded arithmetic mean differential parameter value *<u>3n-2A</u>* = -140 mlrd. calculated from the data shown in Table 2 for five 3-methylalkanes **3e - 3j**. The value of it indicates the **large <u>upfield</u> shift of H-2A proton signal** in 3-methylalkanes **3n** family.

3. 2. 3. 1. 2. The *BSP* values of downfield "near end" α-methylene protons (H-2B) in 3-methylalkanes 3n.

As in the previous section we jointly reviewed all *BSP* value of downfield H-2B protons of all 3-methylalkanes **3e - 3j** (i.e., all *3n-B-2B* parameters), including the shortchain symmetrical 3-methylpentane **3e** and midchain 3-methylhexan **3f** (but without the "wrong" "reverse numbered" "3-methylbutane **3d**"). All 5 sets of values of basic parameters *3n-B-2B* are in a reasonably narrow range from 1.320 to 1.350 ppm. <u>This interval is significantly shifted downfield on the value of the "standard" reference parameter *etal-CH₂* = 1.270 ppm</u>. Such a large downfield shift implies a **relatively large <u>positive</u>** individual differential parameters *3n-2B* value of each **3e - 3j** compounds. The rounded arithmetic mean differential parameter value *<u>3n-2B</u>* = +70 mlrd. calculated from the data shown in Table 2 for five 3-methylalkanes **3e - 3j**. The value of it indicates the relatively **large <u>downfield</u> shift of H-2B proton signal** in 3-methylalkanes **3n** family.

3. 2. 3. 1. 3. The *BSP* values of "aggregated" parameters 3n-B-2 (upfield H-2A + downfield H-2B) of "near end" α-methylene protons (H-2) in 3-methylalkanes 3n.

In this section, unlike the previous two, we jointly reviewed all *BSP* values of all 3-methylalkanes **3d - 3j** parameters (i.e., parameters *3n-B-2*), including the "wrong" "reverse numbered" "3-methylbutane **3d**". For the latter, the "wrong" parameters *3n-B-2A* and *3n-B-2B* will take equal in magnitude and equal to 1.200 ppm (see Tables 1 and 2). The calculated values of the individual base parameters *3n-B-2* of the remaining five 3-methylalkanes **3e - 3j** are in a narrow range from 1.220 to 1.245 ppm.

<u>This interval is shifted upfield</u> a relatively small amount from the value of the "standard" reference parameter *etal-CH₂* = 1.270 ppm. Such a relatively small upfield shift implies a **relatively small <u>negative</u>** individual differential parameters *3n-2* value of each of **3e - 3j** compounds. The rounded arithmetic mean

parameter **_3n-2_**, calculated for the five 3-methylalkanes **3e - 3j**, is equal to **_3n-2_ = -35 mlrd.**, indicating that the **relatively small upfield shift** of **"aggregated"** signal of both methylene protons H-2 in 3-methylalkanes **3n** takes place.

In the case of "reverse numbered" "3-methylbutane **3d**", the absolute value of the "wrong" negative "standard" differential parameter value is: **_2d-3_ = _3d-2_** = 1200 − 1270 = **-70 mlrd.**, which is twice the mean parameter value of the above (**_3n-2_ = -35 mlrd.**). This two-fold difference explained by unreasonableness of "wrong" "3-methylbutane **3d**" data inclusion in the number of 5 longchain 3-methylalkanes **3d - 3j** for calculation of the arithmetic mean parameter **_3n-2_**.

3. 2. 3. 2. The *BSP* values of "far end" α-methylene protons (H-4) in 3-methylalkanes 3n.

The proton signals of "far end" α-methylene group $C^4H^4_2$ » ($\delta^{H,3n}_4$) are designated as **_3n-B-4_**. These two protons are <u>magnetically nonequivalent</u> therefore denoted as H-4A and H-4B. All designations are the same as for the notation of the protons H-2A and H-2B.

3. 2. 3. 2. 1. The *BSP* values of upfield "far end" α-methylene protons (H-4A) in 3-methylalkanes 3n.

As in Section 3.2.2., we jointly reviewed all *BSP* values of all 3-methylalkanes **3d - 3j** parameters (i.e., parameters **_3n-B-4A_**), but without the "wrong" "reverse numbered" "3-methylbutane **3d**".

In a symmetrical shortchain 3-methylpentane **3e** the 4 protons of "far end" ($C^4H^4_2$) and "near end" ($C^2H^2_2$) α-methylene groups are equal to each other. They discussed previously (Section 3.2.3.1.2.)

All four individual base parameters **_3n-B-4A_ (n = f ÷ j)** are approximately equal to **1.08 ppm**, and therefore the arithmetic mean base parameter **_3n-B-4A_ = 1.08 ppm**, and the differential mean parameter is equal to **_3n-4A_ = -190 mlrd**. This value **_is very significantly shifted upfield_** relative to a reference parameter **_etal-CH₂_ = _1.270_ ppm**.

3. 2. 3. 2. 2. The *BSP* values of downfield "far end" α-methylene protons (H-4B) in 3-methylalkanes 3n.

The previously considered parameter **_3e-B-2B_ = _3e-B-4B_ = 1.34 ppm** of shortchain symmetrical 3-methylpentane **3e** is no longer being discussed. It seems appropriate to consider jointly the only three parameter values of 3 "true longchain" 3-methylalkanes **3g - 3j** (i.e., parameters **_3n-B-4B_ = 1.23 ÷ 1.24 ppm**, n = g - j). Apart from them we want to discuss the parameter **_3n-B-4B_** of midchain 3-methylhexane **3f** (**_3f-B-4B_ = 1.33 ppm**). We emphasize that the "true longchain" 3-methylalkanes **3g - 3j** parameter values **_3n-B-4B_** (n = g - j) is almost coincided, but are very much different from the same parameter values **_3f-B-4B_** in midchain 3-methylhexane **3f**.

The rounded arithmetic mean differential parameter value **_3n-4B_ = -35 mlrd.** (of n = g ÷ h) indicates a slight upfield shift of the signal of downfield methylene protons H-4B in "true longchain" 3-methylalkanes **3g - 3j**. At the same time, the individual differential parameter **_3f-4B_** is equal to **_3f-4B_ = +10 mlrd.** Because of very small difference from the value of the "standard" reference parameter **_etal-CH₂_ = 1.270 ppm**. this value falls into the "strip of insufficiently validity" of the spectral parameters (**20 mlrd.**). So it is probably not significant.

3. 2. 3. 2. 3. The *BSP* values of "aggregated" parameters 3n-B-4 (upfield H-4A + downfield H-4B) of "far end" α-methylene protons (H-4) in 3-methylalkanes 3n.

For the reasons stated above, we jointly reviewed the *BSP* values of only four of the aggregated parameter **_3n-B-4_** (n = f ÷ j): 3 of "true longchain" 3-methylalkanes **3g - 3j**, as well as" the parameter of midchain 3-methylhexane **3f**.

The calculated values of the three "true longchain" base aggregated parameters *3n-B-4* (n = g ÷ j) are practically the same and are equal to: *3n-B-4* = (1.08 + 1.24)/2 = **1.16 ppm**. The individual aggregated parameter *3f-B-4* = **1.18** ppm, calculated for the midchain 3-methylhexane **3f** differ only slightly. Such a small difference makes it appropriate the calculation of arithmetic mean value of the differential aggregated parameter *3n-4 = -105 mlrd.* all the four terms (n = f ÷ j).

The resulting arithmetic mean value indicates a **fairly significant shift in the strong field** of both **methylene protons H-4 "aggregated" signals** in 3-methylalkanes **3n** family.

3. 3.   The Families of 4-methylalkanes <u>4n.</u>

Table 3 lists given in [2] spectroscopic data of six compounds of 4-methylalkanes **4n** family: two marked with asterisks are "wrong" "reverse numbered" 4-methylalkanes **4n**: 4-methylpentane **4e** (the correct name is 2-methylpentane **2e**), and 4-methylhexane **4f** (the correct name is 3-methylhexane **3f**), as well as four "correct" 4-methylalkanes **4n**: 4-methylheptane **4g**, 4-methyloctane **4h**, 4-methylnonane **4j** and 4-methyldodekane **4k**. In the spectrum of 4-methylnonane **4j**, the authors [2] do not attribute the specific numerical values to the absorption of certain types of methylene protons, and give a fairly wide digital interval (1.24 - 1.32 ppm). And in the spectrum of 4-metildodekane **4k** the authors [2] provide only two digital broad intervals (1.02 - 1.13 ppm) and (1.19 - 1.37 ppm) for absorption of all types of methylene protons.

The "reverse numbered" compound **4e** and **4f** ("correct" **2e** and **3f**) are the most shortchain of all possible 4-methylalkanes **4n**. The result in Table 3 shows the 8 parameter sets for 6 compounds: two sets of "reverse numbered" 4-methylpentane **4e**, two sets of "reverse numbered" 4-methylhexane **4f** and a single set of shown in [2] data of 4 "correct" 4-methylalkanes **4n**. As in the 3-methylalkanes **3n**, some of the methylene protons of the in the 4-methylalkanes **4n** are **magnetically nonequivalent**.

Table 3

The **_base spectral parameters_** (**BSP**) values, i.e. $\delta^{H,4n}_i$ chemical shifts of *i*-type protons of 4-methylalkanes **4n** of the general formula $C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}...\text{-}C^\omega H^\omega_3$

Num-ber of com-pound	Formula	The **BSP** values («$\delta^{H,4n}_i$») in ppm of specified number of "*i*-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.					
		3H 3x[H-1] (t)	1H [H-2A] (m)	1H [H-2B] (m)	1H [H-3A] (m)	1H [H-3B] (m)	1H [H-4] (m)
1	2	3	4	5	6	7	8
4e*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}CH_3$	0.88 (0.880)	1.29 (1.29)	1.29 (1.29)	1.15 (1.15)	1.15 (1.15)	1.54 (1.541)
4f*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)\text{-}CH_3$	0.88 (0.879)	(-) (1.30)	(-) (1.30)	(-) (1.08)	(-) (1.28)	(-) (1.33)
4g	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_2\text{-}CH_3$	(0.877)	(1.26)	(1.26)	(1.08)	(1.34)	(1.41)
4h	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_3\text{-}CH_3$	(0.876)	(1.28)	(1.31)	(1.07)	(1.23)	(1.39)
4j	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_4\text{-}CH_3$	(0.877)	(-)[a]	(1.32)	(1.07)	(1.22)	(1.39)
4k	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_7\text{-}CH_3$	(0.88)	(-)[c]	(-)[c]	(-)[b]	(-)[c]	(1.38)

Continuation of Table 3

		3H 3x[H-4'] (t)	1H [H-5A] (m)	1H [H-5B] (m)	1H [H-6A] (m)	1H [H-6B] (m)	3H 3x[H-ω] (t)
1	2	9	10	11	12	13	14
4e*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}CH_3$	0.865 (0.864)					0.865 (0.864)
4f*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)\text{-}CH_3$	0.845 (0.841)	(-) (1.13)	(-) (1.33)			0.860 (0.857)
4g	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_2\text{-}CH_3$	(0.839)	(1.08)	(1.34)	(1.26)	(1.26)	(0.877)
4h	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_3\text{-}CH_3$	(0.841)	(1.10)	(1.25)	(1.28)	(1.35)	(0.894)
4j	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_4\text{-}CH_3$	(0.840)	(1.10)	(1.24)	(-)[a]	(1.35)	(0.885)
4k	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_7\text{-}CH_3$	(0.839)	(-)[b]	(-)[c]	(-)[c]	(-)[c]	(0.88)

[a] 1.24 - 1.32;   [b] 1.02 – 1.13;   [c] 1.19 – 1.37.

3. 3. 1. The *BSP* values of methyl group protons in 4-methylalkanes 4n.

In the 4-methylalkanes **4n** family (as in 3-methylalkanes **3n**) the "near end" methyl groups $C^1H^1_3$ is not equivalent to the middle ones ($C^{4'}H^{4'}_3$), so the spectral parameters of the ***4n-B-1*** ($\delta^{H,4n}_1$) and ***4n-B-4'*** ($\delta^{H,4n}_{4'}$) are considered separately.

3. 3. 1. 1. The *BSP* values of "near end" methyl group protons (H-1) in 4-methylalkanes 4n.

In the PMR spectrum of 4-methylalkanes **4n** the triprotonic signal of "near end" methyl group $C^1H^1_3$ (i.e., three protons H -1) appears as a distinct triplets and so is easily interpreted. All 8 sets of values of the base parameters ***4n-B-1*** (including the above-considered "wrong" parameters of "reverse numbered" 4-methylalkanes **4n**: ***4e-B-1*** (the correct name is 2-methylpentane **2e**) and ***4f-B-1*** (the correct name is 3-methylhexane **3f**) are in a very narrow (4 **mlrd.**) interval in the range of 0.876 to 0.880 ppm, in which falls also the value of the "standard" reference parameter ***etal-CH₃* = 0.88 ppm**. The nearness of each value ***4n-B-1*** with each other and also to the value of "standard" reference parameter ***etal-CH₃*** means that all 7 individual differential parameters ***4n-1*** to be <u>negligible in magnitude and negative in sign (i.e., practically zero).</u>

In the shortchain "reverse numbered" 4-methylalkanes **4n**: 4-methylpentane **4e** and 4-methylhexane **4f** because the shorteness of second branch of carbon chain, denoted as C-5 - C-ω, both sets of base parameter ***4e-B-1* = *2e-B-5*** = 0.88 (0.880 ppm) and ***4f-B-1* = *3f-B-6*** = 0.88 (0.879 ppm) are shifted (albeit very slightly) downfield compared to the other three parameters ***4n-B-1*** (n = g-j). The arithmetic mean differential parameter ***4n-1*** ($\delta^{H,aver.4n}_1$), calculated from the values of all eight ***4n-B-1*** sets is indeed close to zero. It is equal to ≈ **-1 mlrd.**, rounded: ***4n-1* = 0 mlrd.**

3. 3. 1. 2. The *BSP* values of "far end" methyl group protons (H-ω) in 4-methylalkanes 4n.

The "far end" methyl groups in 4-methylalkanes family **4n** are designated as "$C^{\omega}H^{\omega}_3$". The triprotonic signals manifested as a distinct triplet and easy to interpret. In most longchain ("true longchain") 4-methylalkanes **4n** (for example, **4h**, **4j** and **4k**) the branching at the carbon atom C-4 is located far enough of the "far end" methyl group $C^{\omega}H^{\omega}_3$. It is expected that branching at C-4 virtually no impact on the *BSP* values of three protons H-ω. Within measurement error the parameters ***4n-B-ω*** (as in longchain 2-methylalkanes **2n** and 3-methylalkanes **3n**) in these "longchain" 4-methylalkanes **4n** will be approximately equal the magnitude of "standard" reference parameter ***etal-CH₃* = 0.880** ppm. In formally "the most shortchain 4-methylalkane", the "reverse numbered" 4-methylpentane **4e** and 4-methylhexane **4f** the parameters ***4e-B-ω = 4e-B-5*** and ***4e-B-ω = 4f-B-6*** consideration for the above reasons is inappropriate.

The symmetrical 4-methylheptane **4g**, because of its both chain length (as branching occurs only γ-carbon atom of the chain) is unlikely to be shortchain alkane, rather the midchain compound. It is therefore appropriate to consider it together with the other three "true longchain" 4-methylalkanes **4n**. The individual base parameters ***4n-B-ω*** of this four compounds are different within the measurement error: ***4g-B-7*** = 0.877 ppm ; ***4h-B-8*** = 0.894 ppm, : ***4j-B-9*** = 0.885 ppm and ***4k-B-12*** = 0.880 ppm. The calculated values of these four individual differential parameters ***4n-ω*** and the arithmetic mean differential parameter ***4n-ω***, though is not zero, but has a very small positive value (***4n-ω* = + 5 mlrd.**) , which is much less than the highest measurement error.

3. 3. 1. 3. The *BSP* values of the newly introduced mid methyl group protons (H-4') in 4-methylalkanes 4n.

Mid methyl group in the 4-methylalkanes **4n** are designated as $C^{4'}H^{4'}_3$, and their three protons as H-4'. In the PMR spectrum of 4-methylalkanes **4n** the signal of newly introduced mid methyl group protons (H-4') is clearly manifested in the form of a doublet, so easy to interpret. The *BSP* values of these three protons labeled as ***4n-B-4'*** ($\delta^{H,4n}_{4'}$). The methyl groups $C^{4'}H^{4'}_3$ in the "reverse numbered" 4-methylalkanes **4e** and **4f** were discussed earlier and therefore do not participate in the discussion.

In the "true longchain" 4-methylalkanes **4h, 4j** and **4k** as well as in midchain compound **4g** all 4 parameters **4n-B-4'** are in a very narrow range of 0.839 to 0.841 ppm. This interval is **sufficiently far upfield shifted** from a" standard" reference parameter **etal-CH$_3$ = 0.880 ppm**. Such a large upfield shift implies a relatively large negative individual differential parameters **4n-4'** value of each **4g – 4k** compounds. The arithmetic mean differential parameter **4n-4' = -40 mlrd.** is calculated from the four 4-methylalkanes **4g – 4k** and indicates the **most significant upfield shift of mid methyl group signal** in 4-methylalkanes **4n** family compared with signals of other above-considered methyl groups (even with signal **3n-3' in** 3-methylalkanes **3n**).

3. 3. 2. The *BSP* values of methine protons (H-4) in 4-methylalkanes 4n.

The methine groups in the 4-methylalkanes **4n** are designated as C^4H^4, and their only proton as H-4. In the PMR spectrum of 4-methylalkanes **4n** the signal of methine proton manifests itself as a multiplet, often superimposed on multiplet methylene groups signals (so it is not easy to interpret). The *BSP* values of these proton labeled as **4n-B-4** ($\delta^{H,4n}_4$). The methine protons in the "reverse numbered" 4-methylalkanes **4e** and **4f** were discussed earlier and therefore do not participate in the discussion.

Table 3 lists the four **4n-B-4** discrete values for the PMR spectra of "true longchain" 4-methylalkanes **4h, 4j** and **4k** as well as of midchain compound **4g**. All are within a rather narrow range from 1.38 to 1.41 ppm. The smallest base parameter **4k-B-4 = 1.38** ppm is found in most longchain 4-methyldodekane **4k**. And the most downfield parameter **4g-B-4 = 1.41** ppm of the mentioned range is found for the "shortest" from all "long-chain" compounds (i.e., for midchain symmetrical 4-methylheptane **4g**). It shifted downfield from the other three parameters (**4h-B-4**, **4j-B-4** и **4k-B-4**) to a value of 20 ÷ 30 **mlrd.**, so its individual differential parameter value **4g-4** = **+140 mlrd.** greatest.

The positive values of three "true longchain" differential parameters **4n-4** (n = h ÷ k) are **+110 ÷ +120 mlrd.**, and their rounded arithmetic mean differential parameter **4n-4 = + 115 mlrd.** Taking into account the same and the "midchain" individual parameter **4g-4** = **+140 mlrd.**, the arithmetic mean value of the 4 parameter increases to **4n-4** = **+120 mlrd.**

3. 3. 3. The *BSP* values of methylene protons in 4-methylalkanes 4n.

The signals of methylene protons in PMR spectra of 4-methylalkanes **4n** marked the principle described above. Typically, both two protons of each methylene group are **magnetically nonequivalent.**

3. 3. 3. 1. The *BSP* values of "near end" α-methylene protons (H-3) in 4-methylalkanes 4n.

Two magnetically nonequivalent protons of the "near end" α-methylene group $C^3H^3_2$ are designated as H-3A and H-3B. Table 3 shows the six sets of discrete values of the six **4n-B-3** parameters (one for each of the two magnetically nonequivalent protons H-3) in PMR spectra of the five 4-methylalkanes **4n** (**4f - 4j**). However, the three of previously discussed setting of two "wrong", "reverse numbered" 4-methylalkanes **4e** and **4f** are not discussed here. The **BSP** values of "near end" methylene group protons (H-3) in 4-methyldodecane **4k** also are not discussed for reasons described in the beginning of Section 3.3.

3. 3. 3. 1. 1. The *BSP* values of upfield "near end" α-methylene protons (H-3A) in 4-methylalkanes 4n.

All three sets of discrete values of the basic parameters **4n-B-3A** (**4g-B-3A**, **4h-B-3A**, **4j-B-3A**) are in a very narrow range of values from 1.07 to 1.08 ppm (it is also above-considered "wrong" parameter **4f-B-3A**). This interval is **very significantly shifted upfield** on the value of the "standard" reference parameter **etal-CH$_2$ = 1.270** ppm. Such a large upfield shift implies a relatively large negative individual differential parameters **4n-3A** value of each **4f - 4j** compounds. The rounded arithmetic mean differential parameter value **4n-3A** = **-200 mlrd.** calculated from the data for four 4-methylalkanes **4f – 4j**. The value of it indicates the large upfield shift of H-3A proton signal in 4-methylalkanes **4n** family.

Probably the closest value can be an individual differential parameter **4k-3A** also. It is impossible to calculate the value as specific figures, as in Table 3 the **4k-B-3A** parameter represented as interval (1.02-1.13 ppm). If you enter into the calculation of individual differential parameter **4k-3A** the mean value of the boundaries of this interval (from 1.02 ppm to 1.13 ppm), we get very close to the above value: **4k-3A = -195 mlrd.**

3. 3. 3. 1. 2. The *BSP* values of downfield "near end" α-methylene protons (H-3B) in 4-methylalkanes 4n.

It seems appropriate to consider together the two parameters **4n-B-3B** of "true longchain" 4-methylalkanes **4h** and **4j** and separately from it the parameter **4g-B-3B** of midchain symmetrical 4-methylheptane **4g**.

The **BSP** values of two "true longchain" 4-methylalkanes **4h** and **4j** parameters **4n-B-3B** are practically identical: **4h-B-3B** = 1.23 ppm and **4j-B-3B** = 1.22 ppm (the parameter **4k-B-3B** as said above shows a range of values).These signals are <u>not significantly</u> **shifted upfield** on the value of the "standard" reference parameter **etal-CH₂** = **_1.270_** ppm. Such relatively small upfield shift implies a relatively small negative individual differential parameters **4h-3B = -40 mlrd.**and **4j-3B = -50 mlrd.** The arithmetic mean differential parameter **4n-3B = -45 mlrd.**

For the third the "shortest of long-chain compounds" the symmetrical 4-methylheptane **4g** (which can be properly considered as midchain compound) the **BSP** values (**4g-B-3B = 1.34** ppm) is significantly **shifted downfield** (more than **100 mlrd.** the values of **4h-B-3B** and **4j-B-3B**). Therefore, its individual differential parameter value **4g-3B** = **+70 mlrd.** quite significant and **_positive_** by sign, unlike the arithmetic mean parameter **4n-3B = -45 mlrd**, which is **_negative_** by sign. The reason for this very significant difference of **4n-3B** and **4g-3B** values is unknown to us[3]*.

As before, we choose from two a diametrically opposite values (**4n-3B = -45 mlrd** and **4g-3B = +70 mlrd.**) as the **"typical" values** of low field "near end" α-methylene protons H-3B absorption in 4-methylalkanes **4n** just the <u>arithmetic mean parameter</u> **4n-3B = -45 mlrd**, which is calculated from **BSP** values of two "true longchain" 4-methylalkanes **4h** and **4j**.

3. 3. 3. 1. 3. The *BSP* values of "aggregated" parameters *4n-B-3* (upfield H-3A + downfield H-3B) of "near end" α-methylene protons (H-3) in 4-methylalkanes 4n.

As for the other "aggregated" parameters of the methylene group protons it seems reasonable to jointly consider the computed "aggregated" parameters **4n-B-3** for all five 4-methylalkanes **4e - 4j** listed in Table. 3 (except of 4-methyldodecane **4k**, where due to lack of discrete values of **4k-B-3A** and **4k-B-3B**, the calculation of the "aggregated" parameter **4k-B-3** was impossible.).

For the "wrong" "reverse numbered" 4-methylpentane **4e** the parameters **4e-B-3A** and **4e-B-3B** due to the magnetic equivalence of the two protons are equal in magnitude and equal to 1.15 ppm (see Tables 2 and 3), and hence the value of "aggregated" parameter **4e-B-3** is also equal to 1.15 ppm. The calculated values of "aggregated" base parameters **4n-B-3** of remaining four 4-methylalkanes **4f - 4j** (**4f-B-3** = 1.18 ppm; **4g-B-3** = 1.21 ppm; **4h-B-3** = 1.15 ppm and **4j-B-3** = 1.145 ppm) are located within a relatively narrow (**60 mlrd.**) interval in a range of values from 1.15 to 1.21 ppm. If we exclude the largest in value parameter **4g-B-3** = 1.21 ppm, obtained from the drop-down of a number of parameters **4g-B-3B** = 1.34 ppm (see above) , the interval narrows to 30 **mlrd.** (of 1.15 to 1.18 ppm) .

The rounded arithmetic mean value of differential "aggregated" parameter (**4n-3** = **-105 mlrd.**) , calculated from the individual parameters **4n-3** of five methylalkanes **4e - 4j**, indicates a **_rather large upfield shift of two methylene protons H-3 "sum" signal_** in 4-methylalkanes **4n**. If we exclude from consideration the "anomalous" parameter **4g-B-3** = 1.21 ppm of 4-methylheptane **4g**, then calculated from the remaining four sets of data value (**4n-3** = **-115 mlrd.**) is **even more shifted upfield (to 1.155 ppm) the mean "sum" signal of both methylene protons H-3 in 4methylalkanes 4n family.**

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[3]* *It's possible, the discussed difference in parameter values **4h-B-3B** is connected with an alkyl chain length of 4-methylalkanes **4n**. Among other possible reasons, we consider the probability of finding the wrong center of H-4B proton multiplet signal by authors of [2], or even just a typo.*

3. 3. 3. 2. The *BSP* values of "far end" α-methylene protons (H-5) in 4-methylalkanes 4n.

Table 3 shows 4 sets of four discrete values for the parameters **4n-B-5** ($\delta^{H,4n}_5$) of "far end» α-methylene group $C^5H^5_2$ (one for each of the two magnetically nonequivalent protons H-5) in NMR spectra of **4n** family compounds (**4f - 4j**). In the spectrum of 4-methyldodecane **4k** the absorption signals **4k-B-5** for the protons H-5 are digital intervals.

3. 3. 3. 2. 1. The *BSP* values of upfield "far end" α-methylene protons (H-5A) in 4-methylalkanes 4n.

All three sets of discrete values of the basic parameters **4n-B-5A** are in a narrow interval ranging of 1.08 to 1.10 ppm. The "wrong" "reverse numbered" parameter **4f-B-5A**, entered in the table 3, was discussed earlier.

In the symmetrical midchain 4-methylheptane **4g** the protons of "far end" ($C^5H^5_2$) and "near end" ($C^3H^3_2$) α-methylene groups are equal and are discussed in Section 3.3.3.1.1. The value of this parameter **4g-B-5A = 1.08 ppm** is slightly different from the parameters of the "true longchain" 4-methylalkanes **4h** and **4j** (**4h-B-5A = 4j-B-5A = 1.10 ppm**) in the "typical", i.e., more longchain alkanes **4n**. The values of all three individual parameters **4n-B-5A** are **very much shifted upfield** relative to a reference parameter **etal-CH₂** = _**1.270 ppm**_. Therefore, each individual differential parameter **4n-5A** (n = g ÷ j) and the arithmetic mean parameter _**4n-5A**_ = **-175 mlrd.** a **very large negative value**. Such **very large upfield shift implies a very large negative** individual differential parameters **4n-5A** of the **upfield methylene proton's H-5A** signal in 4-methylalkanes **4n** family.

3. 3. 3. 2. 2. The *BSP* values of downfield "far end" α-methylene protons (H-5B) in 4-methylalkanes 4n.

It seems appropriate to consider jointly the only **4n-B-5B** parameters of the two "true longchain" 4-methylalkanes : **4h** and **4j** (for the "most longchain" 4-methylalkane **4k** due to lack of discrete values of signals in spectrum PMR, the calculation of the parameter **4k-B-5B** was impossible). The parameter **4g-B-5B** of symmetrical midchain 4-methylheptane **4g** is appropriate to discuss them separately. Indeed, the absorption of low-field α-methylene protons (H-3B and H-5B) in a 4-methylheptane **4g** (**4g-B-5B = 4g-B-3B = 1.34** ppm) is significantly different from those of "true longchain " parameters **4h-B-5B = 1.25** ppm and **4j-B-5B = 1.24** ppm, but at the same time substantially equal to the value of the chemical shift of the "wrong" "reverse numbered" parameter **4f-B-5B**, (the correct name is 3-methylhexane **3f**: **3f-B-3B = 4f-B-5B** = 1.33 ppm) . We do not know the reasons for this coincidence[4]*, so, as before, we will discuss only "true longchain" parameters **4h-B-5B** and **4j-B-5B**.

The arithmetic mean base parameter values _**4n-B-5B**_ = 1.245 ppm (when n = g, h) is **shifted upfield** (but not significant) relative to a reference parameter **etal-CH₂** = _**1.270**_ ppm. The individual differential (**4h-5B** and **4j-5B**), as well as the arithmetic mean differential parameters _**4n-5B**_ = **-25 mlrd.** Such **relatively small upfield shift** implies a relatively small **negative** individual differential parameters **4n-5B** of the **downfield methylene proton's H-5B** signal in 4-methylalkanes **4n** family.

The value of the base spectral parameter **4g-B-5B = 1.34** ppm for symmetrical midchain 4-methylheptane **4g**, on the contrary, is **shifted downfield** relative to a reference parameter **etal-CH₂** = _**1.270**_ ppm. Hence the individual differential parameter **4g-5B** has a positive value equal to **+70 mlrd.** The possible reason for this different behavior of downfield methylene protons H-5B absorption in considered 4-methylalkanes **4n** lies in the length of their chains (see above).

So, as before, we choose from two a diametrically opposite values (_**4n-5B**_ = **-25 mlrd** and **4g-5B = +70 mlrd.**) as the **"typical" values** of low field "far end" α-methylene protons H-5B absorption in 4-methylalkanes **4n** just the _arithmetic mean parameter_ _**4n-5B**_ = **-25 mlrd**, which is calculated from *BSP* values of two "true longchain" 4-methylalkanes **4h** and **4j** rather than parameter **4g-5B = +70 mlrd.**

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[4]* *Other possible reasons, we consider the probability of finding the wrong center of H-4B proton multiplet signal by authors of [2], or even just a typo.*

3. 3. 3. 2. 3. The *BSP* values of "aggregated" parameters *4n-B-5* (upfield H-5A + downfield H-5B) of "far end" α-methylene protons (H-5) in 4-methylalkanes 4n.

In this section for the reasons stated above, we jointly reviewed the *BSP* values of the aggregated parameters *4n-B-5* of "true longchain" 4-methylalkanes **4h** and **4j**. The aggregated parameter *4g-B-5* of symmetrical midchain 4-methylheptane **4g** is appropriate to discuss them separately.

The calculated values of the two "true longchain" base aggregated parameters *4n-B-5* (n = h, j) are practically the same and are equal: *4n-B-5* = (1.095 + 1.245)/2 = **1.17 ppm** and **very much shifted upfield** relative to a reference parameter *etal-CH$_2$* = *1.270* ppm. Therefore, each individual differential aggregated parameter *4n-5* (n = h, j) and the arithmetic mean aggregated parameter *4n-5* = **-100 mlrd. large negative value**. The resulting arithmetic mean value indicates a **fairly significant shift in the strong field** of both **methylene protons H-5 of "aggregated" signals** in 4-methylalkanes **4n** family.

In the case of the "anomalous" symmetrical midchain 4-methylheptane **4g**, the calculated value of the base parameter *4g-B-5* = **1.21** ppm. The value of the negative individual differential parameter *4g-5* = **- 60 mlrd.** about a half times less in magnitude than the parameter *4n-5* = **-100 mlrd.** "true longchain" 4-methylalkanes **4h** and **4j**. Therefore the value of the aggregated **absorption of the two protons H-5** in the symmetrical midchain 4-methylheptane **4g** is **less significantly shifted upfield**.

3. 3. 3. 3. The *BSP* values of "near end" (H-2) and "far end" (H-6) β-methylene protons in 4-methylalkanes 4n.

Table 3 shows the 5 sets of discrete "near end" parameter values *4n-B-2* (3 of them are relates to the previously discussed "reverse numbered" compounds **4e** and **4f**, a further one - to symmetrical midchain 4-methylheptane **4g**) and only one set - to "true longchain " parameter *4h-B-2* (because the parameters *4j-B-2A* and both parameters *4k-B-2* indicated no discrete numbers, but intervals). The same situation takes place with parameters *4n-B-6*, where there only two sets of digital values for both protons: in *4g-B-6* and *4h-B-6*. This amount of data is insufficient for a full discussion of the spectral parameters. In addition, because of the difficulty of reference signals of considered protons, given in [2] the numerical values do not appear to be sufficiently reliable. Therefore, we consider the calculation of digital values and discussion of "standard" differential arithmetic mean parameters *4n-2A*, *4n-2B*, *4n-2*, and especially the parameters *4n-6A*, *4n-6B*, *4n-6* impractical.

In Table 3 there is only one of all "true longchain" 4-methylalkanes **4n** full set of discrete base parameters for all β-protons - the set of parameters of 4-methyloctane **4h**: *4h-B-2A* = *4h-B-6A* = 1.28 ppm , *4h-B-2B* = 1.31 ppm and *4h-B-6B* = 1.35 ppm. For 4-methylnonane **4j** the discrete numbers are marked only the values of the chemical shifts of downfield protons: *4j-B-2B* = 1.32 ppm and *4j-B-6B* = 1.35 ppm, whereas parameters of upfield protons (H-2A and H-6A) denotes an interval of values. The same applies to the most longchain 4-methyldodecane **4k**.

Because of the paucity of information we are more likely to conclude that the signals of all β-protons in the 4-methylalkanes **4n** are **shifted downfield** from the reference parameter value *etal-CH$_2$* = *1.270* ppm to a greater or lesser extent. The signals values of upfield β-methylene protons (H-2A and H-6A) **are equal** (at 1.28 ppm) and within the measurement errors do not differ from the reference parameter value *etal-CH$_2$* = *1.270* ppm. The signals of lowfield β-methylene protons (H-2B and H-6B), though not very much, but surely shifted downfield (*4n-2B* ≈ **+45 mlrd.** and *4n-6B* ≈ **+80 mlrd.**). It can be assumed that the downfield shift of "far end" H-6 protons is slightly larger than downfield shift of the "near end" protons H-2.

Therefore, for the assessment calculations (see section 3.5) we will use a value of the arithmetic mean aggregated parameter *4n-2* and *4n-6* equal to the minimum is different from the positive value of inaccuracy of measurements (as **± 20 mlrd.**). Therefore we will accept the rounded value of it equal to: *4n-2* = *4n-6* = +25 mlrd.

3. 4. The Families of 5-methylalkanes <u>5n.</u>

At the sources of information we used for a family of 5-methylalkanes **5n** only in [2] we found the spectral parameters of only one "true longchain" 5-methylnonane **5j**, which is also, by definition, is a symmetrical compound. Table 4 shows also three discussed previously, "reverse numbered" 5-methylalkanes **5n** (**5f**, the correctly named as the 2-methylhexane **2f**; **5g**, the correctly named as the 3-methylheptane **3g** and **5h**, the correctly named as the 4-methyloctane **4h**).

Table 4

The _**base spectral parameters**_ (**BSP**) values, i.e. $\delta^{H,5n}_i$ chemical shifts of _i_-type protons of 5-methylalkanes **5n** of the general formula $C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H\ (C^{5'}H^{5'}_3)\text{-}C^6H^6_2\text{-}\ C^7H^7_2\text{-}...\text{-}C^\omega H^\omega_3$

Number of compound	Formula	The **BSP** values («$\delta^{H,5n}_i$») in ppm of specified number of "i-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.					
		3H 3x[H-1] (t)	1H [H-2A] (m)	1H [H-2B] (m)	1H [H-3A] (m)	1H [H-3B] (m)	1H [H-4A] (m)
1	2	3	4	5	6	7	8
5f*	$CH_3\text{-}(CH_2)_3\text{-}CH(CH_3)_2$	0.89 (0.889)	1.26 (1.27)	1.26 (1.27)	1.26 (1.27)	1.26 (1.27)	1.17 (1.17)
5g*	$CH_3\text{-}(CH_2)_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$	(0.891)	(-)ᵃ	(-)ᵃ	(-)ᵃ	(-)ᵃ	(1.09)
5h*	$CH_3\text{-}(CH_2)_3\text{-}CH(CH_3)\text{-}(CH_2)_2\text{-}CH_3$	(0.894)	(1.28)	(1.28)	(1.28)	(1.35)	(1.10)
5j	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_4\text{-}CH_3$	(0.889)	(1.28)	(1.28)	(1.28)	(1.28)	(1.09)

Continuation of Table 4

		1H [H-4B] (m)	1H [H-5] (m)	3H [H-5'] (d)	1H [H-6A] (m)	1H [H-6B] (m)	2H [H-7] (m)	3H 3x[H-ω] (t)
1	2	9	10	11	12	13	13	14
5f*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)\text{-}CH_3$	1.17 (1.17)	1.52 (1.518)	0.870 (0.867)				0.89 (0.889)
5g*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_2\text{-}CH_3$	(1.23)	(-)ᵃ	(0.845)	(1.14)	(1.35)		(0.891)
5h*	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_3\text{-}CH_3$	(1.25)	(1.39)	(0.841)	(1.07)	(1.23)	(1.28 + 1.35)	(0.894)
5j	$CH_3\text{-}(CH_2)_2\text{-}CH(CH_3)\text{-}(CH_2)_4\text{-}CH_3$	(1.23)	(1.28)	(0.844)	(1.09)	(1.23)	(1.28)	(0.889)

a) 1.22-1.35 м.д.;

3. 4. 1. The *BSP* values of methyl and methine group protons in 4-methylalkanes 4n.

In the PMR spectrum of "true longchain" symmetrical 5-methylnonane **5j** to the absorption of most types of methylene protons authors attribute the same numerical value of 1.28 ppm. We believe that this figure means the center polyprotonic multiplet, which in straight-chain alkanes is called as "methylene hump". Therefore, the signals with a value δ^H = 1.28 ppm will not be discussed. The parameter *5j-B-5* ($\delta^{H,5j}_5$) of single methine proton H-5 in Table 4 is also indicated at 1.28 ppm, so the its discussion also does not seem appropriate. Therefore, by analogy with the β-protons of the 4-methylalkanes **4n** family (see Section 3.3.3.3.), we will accept as the rounded value of the arithmetic mean parameter of 5-H protons equal to: <u>*5n-5* = +25 mlrd.</u>

Let's discuss only the firmly established, in our opinion, the following base parameters. Sixprotonic triplet is the signal of two end methyl groups (due to the symmetry of the molecule **5j**), and belong to three protons H-1 in $C^1H^1_3$ and three protons H-9 in $C^9H^9_3$. So the parameters *5j-B-1* ($\delta^{H,5j}_1$) = *5j-B-9* ($\delta^{H,5j}_9$) = 0.889 ppm. This value is, as expected, falls within the range given in Table 4, the values of the "reverse numbered" parameters *5n-B-1* = 0.889 ÷ 0.894 ppm (wherein n = f - g) for compounds **2f**, **3g** and **4h**. The rounded arithmetic mean base parameter <u>*5n-B-1*</u> = 0.890 ppm corresponds to the value of above-considered similar parameters such as <u>*Nn-B-ω*</u> (where N = 2 - 4) of "far end" methyl groups in 2- (**2n**), 3-

(**3n**) and 4-methylalkanes **4n** (≈ 0.88 ÷ 0.89 ppm). The rounded arithmetic mean differential parameter **_5n-_1 = _5n_-ω = + 10 mlrd.** absolute value is much less then accepted limit of **20 mlrd.**

Three protons H-5' doublet signal of the mid methyl group $C^{5'}H^{5'}_3$ ($\delta^{H,5j}_{5'}$) is denoted by parameter (**5j-B-5' = 0.844** ppm) and corresponds to indicated in Table 5 to "reverse numbered" parameters **5n-B-5'** (**5g-B-5' = 0.845** ppm and **5h-B-5' = 0.841** ppm). This value also corresponds in magnitude to similar parameters at the 3- (**3n-B-3'**) and 4-methylalkanes (**4n-B-4'**, but not 2-methylalkanes **2n**). The parameter (**5f-B-5' ≈ 0.87** ppm) **appears unsuitable** for discussion, since it largely depends on very small number of carbon atoms (1) in shortchain branch of full chain in the "reverse numbered" molecule **5f**, i.e. in the correctly named 2-methylhexane **2f**. The rounded arithmetic mean differential parameter **_5n-5'_ = - 35 mlrd.** calculated for the three compounds **5n**: «the correct one» **5j** and two "reverse numbered» **5g** and **5h**, corresponds to the same arithmetic mean value of differential parameters of the mid three protons signal of the methyl group at the 3- (**3n**) and 4-methylalkanes **4n**.

3. 4. 2. The *BSP* values of α- and β-methylene protons in 5-methylalkanes 5n.

It seems appropriate to discuss the similar (because of the molecular symmetry) parameters of two pairs of magnetically non-equivalent protons (**5j-B-4A**, **5j-B-4B** and **5j-B-6A**, **5j-B-6B**) in two α- methylene group, as well as their aggregated parameters **5j-B-4** ($\delta^{H,5j}_4$) and **5j-B-6** ($\delta^{H,5j}_6$).

As it's seen from Table 4, the parameters **5j-B-4A** = 1.09 ppm and **5j-B-4B** = 1.23 ppm are almost equal to the corresponding parameters of the "reverse numbered" 5-methylalkanes **5g** (**5g-B-4A** = 1.09 ppm, and **5g-B-4B** = 1.23 ppm), and **5h** (**5h-B-4A** = 1.10 ppm, and **5h-B-4B** = 1.25 ppm). The expected exception is too shortchain, the "reverse numbered" 5-methylhexane **5f** (i.e., correctly named as 2-methylhexane **2f**), for which the two protons H-4 (on reverse numbering) too close located at the end of a short branch of carbon chain are **magnetically equivalent** (i.e., **5f-B-4A** = 1.17 ppm and **5f-B-4B** = 1.17 ppm). A slightly different picture is observed for the parameters of "far end" (shortchain) branch of the "reverse numbered" 5-methylalkanes (protons H-6). Here, the comparison is only advisable with the parameters of closest to the "true longchain" molecule: i.e., of "reverse numbered" 5-methyloctane **5h** (correctly named as 4-methyloctane **4h**). Indeed, the **BSP** values of two protons H-6 in the "true longchain" molecule of 5-methylnonane (**5j-B-6A** = 1.09 ppm, and **5j-B-6B** = 1.23 ppm) is approximately equal to the same values of similar parameters of "reverse numbered" (but almost "true longchain") molecule of 5-methyloctane **5h** (**5h-B-6A** = 1.07 ppm and **5h-B-6B** = 1.23 ppm). At the same time, in too shortchain "reverse numbered" 5-methylheptane **5g** (correctly named as 3-methylheptane **3g**) the parameters of both magnetically nonequivalent protons H-6 have significantly different values (**5g-B-6A** = 1.14 ppm, and **5g-B-6B** = 1.35 ppm).

The rounded arithmetic mean value of differential parameters of upfield protons H-4A and H-6A of 5-methylalkanes α-methylene groups **_5n_-4A = _5n_-6A = - 175 mlrd.**, are calculated for only two compounds **5n**: the «correct» 5-methylnonane **5j** and "wrong" "reverse numbered" 5-methyloctane **5h** (and also for the "wrong» of "reverse numbered" 5-methylheptane **5g** but only in the case of "near end" "parameter **_5n-_4A**). The **DSP** values of it have the same order of magnitude with the same negative sign, as the corresponded parameters of upfield protons of "near end" and "far end" α-methylene groups in the 3-methylalkanes **3n** and 4-methylalkanes **4n** (**_3n-_2A = -140 mlrd.**, **_3n-_4A = -190 mlrd.**; **_4n-_3A = -200 mlrd.**, **_4n-_5A = -175 mlrd.**).

The same applies to the **slightly negative** rounded arithmetic mean value of differential parameters of downfield protons H-4B and H-6B of 5-methylalkanes α-methylene groups **_5n_-4B = _5n_-6B = - 40 mlrd.** The **similar in magnitude and sign** are the **DSP** values of the downfield α-proton signals of the α-methylene groups in the 3-methylalkanes **3n** and both α-methylene group in the 4-methylalkanes **4n** (**_3n-_4B = -35 mlrd.**; **_4n-_3B = -45 mlrd.**, **_4n-_5B = -25 mlrd.**). The exception is the parameter **_3n-_2B = +35 mlrd.** the downfield α-proton H-2B of the "near end" α-methylene groups $C^2H^2_2$ in the 3-methylalkanes **3n**, so it is not involved in the calculations.

And finally, let's discuss the aggregated parameters of both types of α-methylene protons (H-4 and H-6) in 5-methylalkanes **5n**. The rounded arithmetic mean value of aggregated differential parameter of both protons H-4 (H-4A and H-4B) of 5-methylalkanes **5n** in "near end" α-methylene groups $C^4H^4_2$ **_5n_-4 = - 110 mlrd.**, are calculated for all four compounds **5n**: the «correct» 5-methylnonane **5j** and "wrong" "reverse numbered" **5f, 5g** and **5h**. It has a **significant negative value**. The same applies to the calculated of

the two compounds **5h** and **5j** "far end" rounded arithmetic mean value of aggregated differential parameter *5n-6* = - 115 mlrd. Similar significant negative values detected at rounded aggregated arithmetic mean of α-protons differential parameters of "far end" methylene groups in other methylalkanes **Nn**: in 3-methylalkanes **3n** and for both α-methylene group in the 4-methylalkanes **4n** (*3n-4* = - 105 mlrd.; *4n-3* = - 105 mlrd., *4n-5* = - 100 mlrd.).

Now we shall say a few words about the **BSP** values of four β-protons (H-3 and H-7) in compound of 5 methylalkanes family **5n**. By analogy with the β-protons of the of 4-methylalkanes **4n** family, we assume the aggregated arithmetic mean values of β-protons H-3 and H-7 differential parameter in family of 5-methylalkanes **5n**, equal to: *5n-3* = *5n-7* = +25 mlrd.

3. 5. Estimation the impact of the methyl substituent introduction in the linear alkane molecule.

We propose the following, logically justified (in our opinion) method of estimating the results of the methyl substituent introduction in the linear alkane molecule to modify all its protons spectral parameters, i.e., the result of the transition from the linear alkanes to methylalkanes.

For this let's summarize **all changes** made to the **basic spectral parameters *Nn-B-i*** of **each proton** in the molecule of the starting **linear alkane** and add to this amount the differences from the "standard" reference parameter ***etal-CH$_3$* = 0.880 ppm** for **each of the three protons of the newly introduced methyl group**. As the each proton parameter ***Nn-B-i*** change let's take the calculated its arithmetic mean differential parameter *Nn-i* (see above). The most appropriate is to use the values of *Nn-i*, calculated for the "true longchain" methylalkanes **Nn**. For two magnetically nonequivalent protons of the methylene group we will take its aggregated parameters. For **protons of methylene groups** whose parameters ***Nn-B-i*** **were not considered higher** we take zero differential parameter value, i.e., ***Nn-i* = 0**. We emphasize that the value of the arithmetic mean parameters used are estimates, i.e., accuracy of each of them we estimate of ± **10 mlrd.** Hence the integrated result of the calculation will be expected to have even less accurate (we assume the existence of error of ± **50 mlrd.**)

In the 2-methylalkanes **2n** family the arithmetic mean differential parameters values *2n-i* (expressed in **mlrd.**) we take the following: *2n-1* = -15; *2n-2* = +250; *2n-3* = -110; *2n-4* = -10; *2n-ω* = + 5 and: *2n-2'* = -15.

For the family of 3-methylalkanes **3n** the parameters *3n-i* following: *3n-1* = -25; *3n-2* = -35; *3n-3* = +65; *3n-4* = -105; *3n-ω* = + 5, and: *3n-3'* = -35.

For the family of 4-methylalkanes **4n** the parameters *4n-i* following: *4n-1* = 0; *4n-2* = +25; *4n-3* = -115; *4n-4* = +115; *4n-5* = -100; *4n-6* = + 25; *4n-ω* = + 5, and: *4n-4'* = -40.

For the family of 5-methylalkanes **5n** the parameters *5n-i* following: *5n-1* = +10; *5n-3* = +25; *5n-4* = -110; *5n-5* = +25 ; *5n-6* = -110; *5n-7* = +25; *5n-ω* = + 10, and: *5n-5'* = -35.

As an example, let's bring the **estimated calculation** of *integral (total) changes* in the ***2n-B-i*** values, occurred when replacing a hydrogen atom H-2 on the methyl group at C-2 in the linear alkane to form 2-methylalkanes **2n**. For three protons H-1 the changes are as follows: 3 x (-15) = **-45 mlrd.**, for a single proton H-2 the change will be **+250 mlrd.**, for two protons H-3 the changes will be: 2 x (-110) = **-220 mlrd.**, for two protons H-4 the changes will be: 2 x (-10) = **-20 mlrd.**, for the three protons H-ω the changes will be: 3 x (+5) = **+15 mlrd.**, for the three proton H-2' the changes will be: 3 x (-15) = **-45 mlrd.** The integral (total) changes, named as *Σ2n-i* will be: -45 +250 -220 -20 +15 -45 = **-65 mlrd.** Namely, the integral value of the spectral changes can be estimated as: *Σ2n-i = -65 ± 50* mlrd.

Similarly, for the family of 3-methylalkanes **3n** the **calculated integral value of spectral changes** designated as *Σ3n-i* are: *-380 ± 50 mlrd.*, for a family of **4n**: *-320 ± 50 mlrd.*, for a family of **5n**: *-360 ± 50 mlrd.*

From these estimations one can see that **all four integral spectral changes are negative** but the absolute values are different: the integral spectral changes of 2-methylalkanes **2n** family is several times less than the other three (**3n, 4n** and **5n**) which are substantially equal. Given the approximate nature of these calculations , we can conclude that the *introduction of a methyl substituent in the linear alkane molecule, leading to the formation of methylalkanes molecule, accompanied by a preferential shift upfield of remaining and newly formed types of proton signals.*

Let's analyze the values of the arithmetic mean of each differential parameter *Nn-i*, that make up the integral value of spectral changes *ΣNn-i* for each N-methylalkanes family. At first let's estimate the terms

that cause *upfield shift*. The **main contribution** to each of them is made a **very large in magnitude and negative in sign** the mean parameters of **α-methylene protons** (≈ *-200 mlrd.* per each α-methylene group). Noticeable, but much smaller contribution brings in newly introduced methyl group (≈*-100 mlrd.* of all three methyl protons).

The **main contribution to the downfield shift** is a term of the remaining hydrogen atom linked at the carbon atom which joins "a methyl substituent", i.e., **methine proton**. It **seems likely** that a **very small downfield shift** could also cause the hydrogen atoms of **β-methylene groups**, but this view may be wrong. The end chain methyl groups and the remaining methylene group not virtually cause appreciable displacement in any direction.

These observations explain the multiple difference in the **integral value of spectral changes *Σ2n-i*** of 2-methylalkanes **2n** chemical shifts with one hand and the remaining methylalkanes **Nn** (**N** = 3,4,5) on the other. In molecules of 2-methylalkanes **2n there is only one α-methylene group** $C^3H^3_2$ which causes *upfield shift* (≈ *-200 mlrd.*), while in the remaining three families of methylalkanes **3n**, **4n** and **5n there are two α-methylene groups** (so: 2 x ≈ *-200 mlrd. ≈ -400 mlrd.*). On the other hand the absorption of methine proton (≈ *+250 mlrd.*) is much greater shifts downfield the integral spectral change *Σ2n-i* of the chemical shifts in the 2-methylalkanes **2n** family compared with the same parameters of other methylalkanes (from *5n-5* = **+25 mlrd.** to *4n-4* = **+115 mlrd.**). The *cumulative effect of these two opposing factors* (at approximately constant other factors) *causes the observed results.*

In the family of 2-methylalkanes **2n** the carbon atoms in which there are branching is C-2 (*i* = 2). Therefore the most interesting to us is *tetracarbonic fragment* (and nonahydrogenic) **[$C^{i-1}H^{i-1}_3$-$C^iH^i(C^{i'}H^{i'}_3)$–$C^{i+1}H^{i+1}_2$-]** (where *i* = 2). For other families of dimethylalkanes **Nn** (**N** = 3, 4, 5) the very similar tetracarbonic (and already octahydrogenic!) fragments **[-$C^{i-1}H^{i-1}_2$-$C^iH^i(C^{i'}H^{i'}_3)$–$C^{i+1}H^{i+1}_2$-]** appear at a branching point, which gradually move to mid of chain. From the above it can be seen *that just this fragment of molecule provides almost all "aggregated" (integral) spectral changes ΣNn-i* that occurred during the conversion from linear alkanes **n** (not containing methyl substituents) to monomethylalkanes **Nn** (in process **n → Nn**).

4. General conclusions.

1. We have analyzed the protons chemical shifts values in the NMR spectra of methylalkanes compounds of general formula **Nn** (when **n** is the letter designation of linear alkane, and **N** is the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**). It is calculated the individual (*Nn-i*) and arithmetic means (*Nn-i*) "standard" differential parameters (the difference between absorption of studied proton in **Nn** and its absorption in the **n**). It is calculated the differences between the total values of *Nn-i* parameters for **all protons in the molecule** of **Nn**. These values are called the "integral spectral changes" that occur in process **n → Nn**, and designated as **Σ Nn-i**.

2. All four types of the sum parameter **ΣNn-i** that occur when into alkane molecule **n** are introduced methyl groups (i.e., in the **n → Nn** process) **are negative (upfield)** but notably *differ in magnitude*. (**Σ Nn-i < 0**)

3. The values of the sum parameter (**Σ Nn-i** = **-65 ± 50 mlrd.**) of dimethylalkanes **2n** families (when **N = 2**) is **much less** three types of "longchain" families of dimethylalkanes **Nn** (when **N** = 3, 4, 5) (**Σ Nn-i = -350 ± 30 mlrd.**).

References

[1] Mizyuk V. and Shibanov V. Proceed. 16th Int. Electronic Conf. on Synthetic Organic Chemistry (ECSOC-16), 2012
[2] www.aist.go.jp
[3] Aldrich/ACD Library of FT NMR Spectra (Pro) Data Base Window.