Volodymyr Mizyuk and Volodymyr Shibanov

The influence of the second methyl group position on the chemical shifts values of all protons in dimethylalkane molecules in the ^{1}H NMR spectra.

Ukrainian Academy of Printing, Lviv, Ukraine

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Abstract. The protons chemical shifts values in the PMR spectra of dimethylalkanes of general formula **N^1,N^2-n** (when **n** is the letter designation of linear alkane, and **N^1, N^2** are the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**) have analyzed. It is calculated and discussed the individual (***N^1,N^2-n-i***), the arithmetic means (***N^1,N^2-n-i***) "standard" differential parameters (the difference between absorption of studied proton in **N^1,N^2-n** and its absorption in the **n**) and the "integral spectral changes" **Σ *N^1,N^2-n-i*** that occur in process **n → N^1,N^2-n**). Also it is calculated and discussed the individual (***N^1,N^2-n′-i***) and the arithmetic means (***N^1,N^2-n′-i***) additional differential parameters (the difference between absorption of studied proton in **N^1,N^2-n** and its absorption in the correspondent monomethylalkane **Nn**) of dimethylalkanes **N^1,N^2-n.**

Keywords: chemical shift, base spectral parameters, "standard" and additional differential parameters, linear alkanes, methylalkanes, dimethylalkanes, 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 study of chemical shift values of all protons in the monomethylalkanes molecules. The next step is planned to study the effect of the introduction of a second methyl group in the alkyl chain of the monomethylalkanes on NMR spectral parameters of resulted dimethylalkanes molecules. It was shown for all the studied types of monomethylalkanes that the introduction of a methyl group at different positions of the alkyl chain leads to approximately the same result: significantly changed only proton chemical shifts of the so-called "tetracarbonic fragment" $[-C^{n-1}H^{n-1}{}_2-C^nH^n(C^{n'}H^{n'}{}_3)–C^{n+1}H^{n+1}{}_2-]$. There are two such "tetracarbon fragments" in dimethylalkanes molecules. It is interesting to examine the change in the PMR spectra as the result of the interaction between these fragments when they change their relative position in the molecule.

1.2. Objects of research

Generally designated each molecule of dimethylalkane ««**N^1,N^2-n»** consists of two parts: the first two numeric of the **N^1** and **N^2** (**$N^2 \geq N^1$**) separated by commas indicates the position of two methyl groups in the alkyl chain (i.e., specified family of dimethylalkanes). Then, with a hyphen small letter indicate the name of the alkane. Numbering started with the shortest chain of methane ("a"), although among considered dimethylalkanes there are no derivative of methane "a" and ethane «b». The symbol "c" denotes propane, «d»- butane, «e»- pentane, «f»- hexane, «g» - heptane and «h»- octane. The different isomers of dimethylalkanes are formed depending on the occurrence place of both methyl groups in the chain («**N^1**» and «**N^2**»). "Near end" methyl group is marked by the number **N^1**, and "far end" – by the number **N^2**. For example, 2,5-dimethyloctane denoted as «**2,5-h**».This example shows the numbering of carbon and hydrogen atoms in all of the families of «**N^1,N^2-n»**dimethylalkanes.

For instance, the compounds of «**2,5-n**» family have the structure:

$$C^1H^1{}_3\text{-}C^2H^2(C^{2'}H^{2'}{}_3)\text{-}C^3H^3{}_2\text{-}C^4H^4{}_2\text{-}C^5H^5(C^{5'}H^{5'}{}_3)\ldots\text{-}C^{\omega-1}H^{\omega-1}{}_2\text{-}C^{\omega}H^{\omega}{}_3$$

The monomethylalkanes molecules consist some several types of one-carbonic fragments: the two "end" and one "mid" methyl groups, "methine-type" carbon atom and several types of methylene groups, which differ one other depending on the position in the chain. Each of these "monocarbonic fragments" can be either in the "short-chain" fragment or in the "long-chain" fragment of carbon chain. «Short-chain" fragment comprises less number of carbon atoms from the beginning of the chain to its branching (i.e., to "methine" carbon atoms bonded to "methyl substituent") than the "long-chain" fragment. In symmetrical molecules such concepts are meaningless. Together with the multiple types of "monocarbonic fragments" as described above [1], one of the dimethylalkane family's **N^1,N^2-n** (namely the gem-dimethylalkanes when **N^1** = **N^2**) contains a new monocarbonic fragment. This fragment is a quaternary carbon atom.

In some cases, the two of "one-carbonic fragments" should be viewed jointly as a single "dicarbonic" moiety, such as shown in the above example so-called " methine fragment" [-$C^2H^2(C^{2'}H^{2'}{}_3)$-]. A new types of "carbonic fragments" so called "three-carbonic gem-dimethyl moiety" [-$C^n(C^{n'}H^{n'}{}_3)(C^{n''}H^{n''}{}_3)$-] adds to other "carbon fragments" only in the families of gem-dimethylalkanes.

In alkyl chain of each type of dimethylalkane families **N^1,N^2-n** the number of each carbon atom (as well as hydrogen atoms bonded to it) is denote the numeral «***i***». The "mid" methyl groups designated of «***i***» numeral of such carbon atom in the chain to which they are bonded, with the addition of dash (or with addition of two dashes to the second methyl group in gem-dimethylalkanes). For example, each of three hydrogen atoms of "far end" methyl group (-$C^{5'}H^{5'}{}_3$) which is bonded to an atom C-5 in 2,5-dimethyloctane «**2,5-h-5'**», are designated as H-5' . Accordingly, the proton chemical shift of this methyl group is indicated (see below) as «$\boldsymbol{\delta}^{\mathbf{H,2,5\text{-}h}}{}_{\mathbf{5'}}$». In gem-dimethylalkanes (for example, 3,3-dimethylheptane **3,3-g**) both "mid" methyl groups denoted as «-$C^{3'}H^{3'}{}_3$» and «-$C^{3''}H^{3''}{}_3$», and their carbon and hydrogen atoms as: C-3', C-3'', H-3' and H-3''.

In the information sources used by us [2, 3] lack the spectral data for such longchain dimethylalkanes that contain "near end" methyl group only at C-5 (**N^1** = 5) or longer in the chain. Therefore, our analysis is limited to a few families up to **4,N^2**-dimethylalkanes (**4,N^2-n**).

Signal of proton in molecule of dimethylalkane «**N^1,N^2-n**» in general designated as «$\boldsymbol{\delta}^{\mathbf{H,N1,N2\text{-}n}}{}_{i}$». In superscript part we consistently separated by a comma, specify: a) the type of the spectrum (H - proton spectrum), b) the number of substance - **N^1,N^2-n**; 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 «one-carbonic fragment" «***i***» in the alkyl chain). In every methylene groups each of two protons may be (or may not be!) **magnetically equivalent**. In the case of magnetic non-equivalence the upfield ("highfield") proton is designated by the letter "A", and its signal as $\boldsymbol{\delta}^{\mathbf{H,N1,N2\text{-}n}}{}_{\boldsymbol{iA}}$ and downfield ("lowfield") – by the letter "B" ($\boldsymbol{\delta}^{\mathbf{H,N1,N2\text{-}n}}{}_{\boldsymbol{iB}}$). For example, "far end" α- methylene protons H-6A and H-6B in 3,5-dimethyloctane **3,5-h** denoted as $\boldsymbol{\delta}^{\mathbf{H,3,5\text{-}h}}{}_{\boldsymbol{6A}}$ ("upfield" proton), and "lowfield" as $\boldsymbol{\delta}^{\mathbf{H,3,5\text{-}h}}{}_{\boldsymbol{6B}}$. The absorption or ***magnetically equivalent*** protons (for example, $\boldsymbol{\delta}^{\mathbf{H,3,5g}}{}_{\boldsymbol{4}}$), or ***"total" absorption two magnetically nonequivalent protons*** (for example, $\boldsymbol{\delta}^{\mathbf{H,2,5g}}{}_{\boldsymbol{3}}$***,*** see below) is denoted without the use of the signs " A" and "B".

Initially we discuss all five families of dimethyl-substituted alkanes **2,N^2-n**, then a compound of families "**3,N^2-n**" and, finally, "**4,N^2-n**». First of all we shall consider such dimethylalkanes, in which the second methyl group is as far away from the first methyl group (the number **N^2** is the maximal). Then the family with lower per unit **N^2**, etc., to the gem-dimethylalkanes when **N^1** = **N^2**.

The discussion of spectral parameters for each of the ***i***- type protons in all of the dimethylalkane ««**N^1,N^2-n»** is produced by the following scheme . The first we examine the three protons of the methyl groups **basic spectral parameters** (***BSP***, see below): a) of "near end", b) of "far end", c) of the two "mid" methyl groups – first one that is closer to the beginning of the chain, then the one that is located farther away. Then we discuss methine protons ***BSP***. Finally, at least we consider the ***BSP*** values of two "methylene" protons in some methylene groups of the molecule. The first we examine the ***BSP*** values of two protons of "near end" α-methylene groups of molecule, then 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" parameter was 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 dimethylalkane **N^1,N^2-n** are arranged in a fairly narrow (1 ppm) range values δ^H: from 0.70 ppm to 1.70 ppm The most easily interpreted are triplet signals of methyl end groups, the signals middle methyl groups (doublets) and the singlet signals of six protons in gem-dimethyl groups (or of nine protons in the compounds **2,2-n**). 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 dimethylalkanes of **2,N^2-n**, **3,N^2-n** and **4,N^2-n** families, denoted above as "$\boldsymbol{\delta}^{\mathbf{H,N1,N2\text{-}n}}_i$", are shown in tables 1-4 situated at the beginning of some sections. These values are called by us the <u>**basic spectral parameters**</u> (shortly, ***BSP***) of protons absorption. If the ***BSP*** value ($\boldsymbol{\delta}^{\mathbf{H,N1,N2\text{-}n}}_i$) is used in both sources [2 and 3] , both figures given in the table. Also, in some tables re-are shown ***BSP*** values for previously cited data of the compounds with reverse numbered carbon chain. Such "reversibly numbered" compounds indicated in Tables by an asterisk (see below).

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 the "***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 **N^1,N^2-n**. 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 [2] 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 $\Delta\delta^{\mathbf{H,N1,N2\text{-}n}}_i$, along with the ***BSP*** values used for the convenience in discussing of the results. About ***DSP*** in detail we will 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 **2,N-n** – **4,N-n**, 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).

3. Discussion of results

As mentioned above, the chemical shift of the studied proton (i.e., its ***BSP***) in the common designation system referred to as "$\delta^{\mathbf{H,N1,N2\text{-}n}}_i$" with using an superscript and subscript symbols. For convenience to simplify the designation due to the failure of an superscript and subscript symbols, in this report <u>***we introduce a new system of designation***</u> <u>for each parameter $\delta^{\mathbf{H,N1,N2\text{-}n}}_i$</u>. In each case the new introduced designation is duplicated the old one (i.e., with using of common superscript and subscript symbols such as "$\delta^{\mathbf{H,N1,N2\text{-}n}}_i$"). The ***BSP*** values ("$\delta^{\mathbf{H,N1,N2\text{-}n}}_i$") in the text and Tables 1 – 4 are marked with italic black bold font as "***N^1,N^2-n-B-i***". The <u>symbol "***B***" indicates that this parameter is basic (</u>***BSP***), and it introduced in order <u>to distinguish the basic parameter from similar</u> abbreviations for the <u>differential spectral parameters</u> (***DSP***). In the above example of the 2,5-dimethyloktane **2,5-h** the symbol «***2,5-h-B-5'***» ($\boldsymbol{\delta}^{\mathbf{H,2,5\text{-}h}}_{5'}$) denotes the magnitude of the chemical shift of the methyl protons **H-5'** of "far end" methyl group - **C$^{5'}$H$^{5'}_3$**. For all or most of the compounds of each the families dimethylalkanes **N^1,N^2-n** we calculated <u>the arithmetic mean value</u> [1] of the discussed parameter referred to as the <u>***underlined***</u> symbol«<u>***N^{1}N^2-n***</u>***-B-i***».

[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.*

The difference between the chemical shift of the every ***i***-th proton in discussed dimethylalkane **N^1,N^2-n** and the same ***i***-th type of protons in the "standard compound", which we denote as (***etal***), we designate as the **differential spectral parameter** «$\Delta\delta^{H,N1,N2-n}{}_i$» (abbreviated ***DSP***). Depending on tasks it may be selected the ***different reference compounds***. The ***DSP*** parameters of all of the discussed dimethylalkanes **N^1,N^2-n** are calculated for each of the ***i***- type proton as follows: $\Delta\delta^{H,N1,N2-n}{}_i = \delta^{H,N1,N2-n}{}_i - \delta^{H,etal}{}_i$, and in our proposed system of notation as : ***N^1,N^2-n-D-i*** = ***N^1,N^2-n-B-i - etal-B-i***.

It is known that in every linear alkanes are present only two types of "one-carbonic fragment». There are the "end methyl group" and "mid methylene group". For protons of these groups previously [1], we determine 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 "triprotonic" signal of each of the methyl groups in the investigated dimethylalkanes **N^1,N^2-n** 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*** values we named as **'standard'** and denote a shorter red bold italic symbol: (***DSP* = *N^1,N^2-n-I*** instead of «***N^1,N^2-n-D-i***»), wherein no letter «D». The **"standard"** differential parameters of **methyl group protons** is calculated as follows ***N^1,N^2-n-i* = *N^1,N^2-n-B-i* – 0.880 ppm** (or: $\Delta\delta^{H,N1,N2-n}{}_i = \delta^{H,N1,N2-n}{}_i - \delta^H{}_{end.} = \delta^{H,N1,N2-n}{}_i - 0.880$ ppm). If the compared signal ***N^1,N^2-n-B-i*** ($\delta^{H,N1,N2-n}{}_i$) is located in a stronger field than the standard signal (**$\delta^H{}_{end.}$= 0.880ppm**), the parameter ***N^1,N^2-n-I*** has the sign "minus" and vice versa. Similarly, the **"standard"** differential parameters of methylene and methine protons is calculated as follows : ***N^1,N^2-n-i* = *N^1,N^2-n-B-i* – 1.270** ppm (or $\Delta\delta^{H,N1,N2-n}{}_i = \delta^{H,N1,N2-n}{}_i$ **– 1.270 ppm**) and has the same signs. The values of "standard" differential parameters ***DSP* = *N^1,N^2-n-I*** expressed in billionths parts (**mlrd.**), i.e. $\Delta\delta^H$ x 1000.

In addition to **"standard"** ***DSP*** sometimes be used other **"additional"** type of ***DSP***, with blue color and with a stroke, that is, ***DSP'* = *N^1,N^2-n'-i***. As the "etalon" compound to calculate this type of ***DSP*** we usually use the "family" of corresponding monomethyl alkanes. As the value of "etalon parameter" is usually taken is the arithmetic mean of ***BSP***, which in [1] is designated as ***N-B-i***. Hence: ***DSP'*** = ***N^1,N^2-n-B-i* - *N-n-B-i***.

The **measurement error** of ***BSP*** values is adopted by us equal to **20mlrd.** 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 groups ***BSP*** 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) should be considered as "insufficiently valid" [2*]. Hence the differential parameters of ***DSP*** and ***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".

3.1. The Families of 2,N-dimethylalkanes 2,N-n

To calculate the family of 2,N-dimethylalkanes **"additional"** values of ***DSP'***, let us bring to mind the arithmetic mean parameters of the "standard" ***DSP*** (***2n-i***, expressed in **mlrd.**),which were calculated for a family of mono-2-methylalkanes **2n** [1]:]: ***2n-1*= -15**; ***2n-2*** **= +250**; ***2n-3*** **= -110**; ***2n-4*** **= -10**; ***2n-ω*** **= + 5** and ***2n-2'*= -15**.

NMR ^{1}H spectra of 2,N-dimethylalkanes which contain the most "remote" second methyl group (at **N^2** = 6), were considered first. Then, gradually , "bringing closer" a second methyl group to first one we reach to the "vic-location" in the 2,3-dimethylalkanes **2,3-n** and finally to the "gem-location" in the 2,2-dimethylalkanes **2,2-n**. In both this families of 2,N-dimethylalkanes is expected no significantly impact the second methyl group on the values of ***BSP*** studied fragments.

3. 1. 1. The family of 2,6-dimethylalkanes 2,6-n

In the family of 2,6-dimethylalkanes **2,6-n** the carbon atoms in which there are branching (C-2 and C-6), are separated by three methylene groups **($-C^3H^3{}_2-C^4H^4{}_2-C^5H^5{}_2-$)**. Therefore, the two of most interesting to us tetracarbonic fragments **[$-C^{i-1}H^{i-1}{}_2-C^iH^i\ (C^{i'}H^{i'}{}_3)-C^{i+1}H^{i+1}{}_2-$]**, (where ***i*** = 2 or 6) [1] does **not overlap one another** , as **separated by one methylene group**, **$-C^4H^4{}_2-$**. So for a family of 2,6-dimethylalkanes **2,6-n** you can expect the almost complete lack of influence of the second methyl group (at C-6) on the value of

BSP studied in this section of the molecule fragment **C-1 - C-4** The second fragment of the molecule, starting from the C-5, which was influenced by the methyl substituent at C-6, in case of need can be considered in other sections.

Table 1 shows the proton ***BSP*** values of two compounds which can be interpreted as 2,6-dimethylalkanes **2,6-n**. This is a "true" 2,6-dimethyloktane **2,6-h** and is not formally related to the 2,6-dimethylalkanes **2,6-n** squalane (2,6,10,15,19,23-hexamethyltetrakosane) marked as "**2,6,10.**“. It covers only the protons ***BSP*** values of the first (of five), a hexacarbonic fragments (C-1 -C-5). For each substance in the Table are two interpretations of spectral data given in [2]: author (in parentheses thin type) and our(the bracketed in bold).

Table 1

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

Number of compound	formula	The (***BSP***) values («$\delta^{H,2,6\text{-}n}_{i}$») in ppm of specified number of “***i***-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.								
		3H 3x[H-1] (d)	1H [H-2] (m)	3H 3x[H-2'] (d)	1H [H-3A] (m)		1H [H-3B] (m)	1H [H-4A] (m)	1H [H-4B] (m)	1H [H-5A] (m)
2,6-h	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	(0.869)	(1.526)	(0.869)	(1.23)	(1.29)	(1.15)			(1.08)
2,6-h	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	**[0.869]**	**[1.526]**	**[0.869]**	**[1.15]**		**[1.26]**			**[1.08]**
2,6,10.	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}$	(0.868)	(1.519)	(0.868)	(1.26)		(1.15)			(1.26)
2,6,10.	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}$	**[0.868]**	**[1.519]**	**[0.868]**	**[1.15]**		**[1.26]**			**[1.08]**

Continuation of Table 1

Number of compound	Formula	The (***BSP***) values («$\delta^{H,2,6\text{-}n}_{i}$») in ppm of specified number of “***i***-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.							
		1H [H-5B] (m)	1H 1x[H-6] (m)	3H 3x[H-6’] (d)	1H [H-7A] (m)	1H [H-7B] (m)	2H [H-8] (m)	2H [H-9] (m)	3H 3x[H-ω] (t)
2,6-h	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	(1.26)	(1.29)	(0.846)	(1.15)	(1.34)			(0.857)
2,6-h	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	**[1.26]**	**[1.29]**	**[0.846]**	**[1.15]**	**[1.34]**			**[0.857]**
2,6,10.	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}$	(1.26)	(1.37)	(0.845)	(1.26)		(1.08)	(1.26)	(0.868)
2,6,10.	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}(C^{6'}H^{6'}_{3})\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}$	**[1.26]**	**[1.37]**	**[0.845]**	**[1.08]**		**[1.26]**	**[1.08]**	**[0.868]**

Let us calculate the "standard» ***DSP*** (***2,6-h-i***) and "additional” ***DSP’*** (***2,6-h’-i***) differential parameters of protons at C-1 - C-4 fragment (***i*** =1÷4) in 2,6-dimethyloktane **2,6-h** and squalane "**2,6,10.**“(***2,6,10.-i*** and ***2,6,10’.-i***, respectively) from the data presented by the authors [2] (authors interpretation of spectra signals).

The “standard“ ***DSP*** values (***2,6-h-i***) of 2,6-dimethyloktane **2,6-h** are: ***2,6-h-1*** = -11 **mlrd.**; ***2,6-h-2*** = +256**mlrd.**; ***2,6-h-2’*** = -11**mlrd.**; (***2,6-h-3A*** = -40**mlrd.**; ***2,6-h-3B*** = +20**mlrd.**); ***2,6-h-3*** = -10**mlrd.**; ***2,6-h-4*** = -120**mlrd.** The “standard” ***DSP*** (***2,6,10.-i***) of squalane ”**2,6,10.”** are: ***2,6,10.-1*** = -12**mlrd.**; ***2,6,10.-2*** = +249**mlrd.**; ***2,6,10.-2’*** = -12**mlrd.**; ***2,6,10.-3*** = -10**mlrd.**; ***2,6,10.-4*** = -120**mlrd.**

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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.*

The "additional" ***DSP'*** values (***2,6-h'-i***) of 2,6-dimethyloktane **2,6-h** are: ***2,6-h'-1*** = +4**mlrd.**; ***2,6-h'-2*** = +6**mlrd.**; ***2,6-h'-2'***= +4**mlrd.**; ***2,6-h'-3A*** = +70**mlrd.**; ***2,6-h'-3B*** = +130**mlrd.**; ***2,6-h'-3*** = +100**mlrd.**; ***2,6-h'-4*** = -110**mlrd.** The "additional" ***DSP'*** (***2,6,10'.-i***) of squalane "**2,6,10.**" are: ***2,6,10.'-1*** = +3**mlrd.**; ***2,6,10.'-2*** = -1**mlrd.**; ***2,6,10.'-2'***= +3**mlrd.**; ***2,6,10.'-3*** = +100**mlrd.**; ***2,6,10.'-4*** = -110**mlrd.**

Let us comment the values of some ***BSP*** and the calculated values of ***DSP*** and ***DSP'***. The values of six methyl protons (three H-1 and three H-2') in mono-2-methylalkanes **2n** and 2,6-dimethylalkanes **2,6-n** are approximately the same and equal to 0.870 ppm. Hence the value of «standard» ***DSP*** is also approximately the same and so the values of "additional » ***DSP'*** are practically zero. The ***BSP*** parameters of methine proton H-2 doublet signal (BSP ≈ 1.520 ppm) in 2,6-dimethylalkanes **2,6-n** also are virtually unchanged compared to similar signals in mono-2-methylalkanes **2n**. Namely, the **introduction of additional methyl group to the C-6 atom, as expected, almost no effect** on the ***BSP*** values of molecule fragment comprising atoms C-1 - C-2 (i.e., six methyl H-1 and H-2' protons and a methine proton H-2), since the second methyl group (**N^2**= 6) **is too far from** the considered protons to **have a marked effect on** their ***BSP*** values.

In the case of author's signal assignment [2] of methylene groups $C^3H^3{}_2$ и$C^4H^4{}_2$ protons the **opposite situation** occurs in respect of the spectral parameters in 2,6-dimethyloktane **2,6-h** and squalane "**2,6,10.**" on the one hand, and similar parameters of mono-2-methylalkanes **2n** on the other hand. The **absolute values of "additional"** ***DSP'*** of 2,6-dimethyloktane **2,6-h** (***2,6-h'-3*** = +100**mlrd.**; ***2,6-h'-4*** = -110**mlrd.**) and squalane (***2,6,10.'-3*** = +100**mlrd.**; ***2,6,10.'-4*** = -110**mlrd.**) **have values approximately equal** to ***100 mlrd.***, although it was expected that they would be close to zero.

This discrepancy led us to offer our own, more logical, in our opinion, assignments of H-3 and H-4 proton signals. It seems logical that the correct assignment of the signals discussed in 2,6-dimethyloktane **2,6-h** and squalane "**2,6,10.**" should correlate with the author's attribution of similar signals for 2-methylalkanes **2n**, presented in the Table 1 in [1] . Therefore our classification, also shown in Table 1, eliminate these differences and ***DSP'*** values for protons H-3 (***2,6-h'-3*** = ***-10*****mlrd.**; ***2,6,10.'-3*** = ***-10*****mlrd.**) and H-4 (***2,6-h'-4*** = ***0*****mlrd.**; ***2,6,10.'-4*** = ***0*****mlrd.**) are close to zero.

When using our assignments, all spectral parameters (basic and differential), of "tetracarbonic fragment" [$-C^1H^1{}_2-C^2H^2(C^{2'}H^{2'}{}_3)-C^3H^3{}_2-$] at the 2,6-dimethylalkanes **2,6-n** correspond to the previously discussed [1] the same parameters of the same fragment in 2-monomethylsubstituted alkanes - **2n**. This confirms the assumption that the lack of effect of the second methyl group (at C-6) on the value of the ***BSP*** of studied in this section fragment of the molecule C-1 - C-4 .

3. 1. 2.The family of 2,5-dimethylalkanes 2,5-n.

In the family of 2,5-dimethylalkanes **2,5-n** the carbon atoms in which there are branching (C-2 and C-5), are separated by two methylene groups fragment **($-C^3H^3{}_2-C^4H^4{}_2-$)**. Therefore, the two of most interesting to us tetracarbonic fragments **[$-C^{i-1}H^{i-1}{}_2-C^iH^i\ (C^{i'}H^{i'}{}_3)-C^{i+1}H^{i+1}{}_2-$]**, (where ***i*** = 2 or 5) [1] does **not overlap one another**, but **"touching each other"**. So for a family of 2,5-dimethylalkanes **2,5-n**, as for 2,6-dimethylalkanes **2,6-n**, you can expect the almost complete lack of influence of the second methyl group (at C-5) on the ***BSP*** value of studied in this section molecular fragment **C-1 - C-3** . Except the symmetrical 2,5-dimethylhexane **2,5-f**, the second fragment of molecules in 2,5-dimethylalkanes **2,5-n** family [$-C^4H^4{}_2-C^5H^5(C^{5'}H^{5'}{}_3)-C^6H^6{}_2-$], can be considered in other sections.

In used sources of information [2,3] we can found ^1H NMR spectra only for two 2,5-dimethylalkanes **2,5-n**: for symmetrical 2,5-dimethylhexane **2,5-f** [2,3] and for asymmetrical 2,5-dimethylheptane **2,5-g** [2]. Both spectra in [2] are obtained by the low-frequency 90MHz instrument, and author's reference of spectra signals are questionable, since they are not confirmed by the data of 400 MHz instrument. Base parameter values ***2,5-f-B-i*** of symmetrical 2,5-dimethylhexane **2,5-f** (according to the authors assignment) as follows (in ppm): ***2,5-f-B-1*** = ***2,5-f-B-2'*** = ***2,5-f-B-5'*** = ***2,5-f-B-6*** = 0.873; ***2,5-f-B-2*** = ***2,5-f-B-5*** = 1.48; ***2,5-f-B-3A*** = ***2,5-f-B-4A*** = 1.14; ***2,5-f-B-3B*** = ***2,5-f-B-4B*** = 1.17. Our assignment of signals in the spectrum of 2,5-dimethylhexane **2,5-f**, given in [3], generally corresponds to authors [2] one, except the multiplet signal of 1.10-1.20 ppm, which we were unable to reliably interpret. Therefore, the discussion will use the attribution of authors [2].

For asymmetrical 2,5-dimethylheptane **2,5-g** there are all only 4 digits in [2] (you can assume that they are the centers of multiprotic multiplet signals) that express all the values ***2,5-g-B-I*** (in ppm) : ***2,5-g-***

B-1 = ***2,5-g-B-2'*** = 0.88; ***2,5-g-B-2*** = 1.39; ***2,5-g-B-3A*** = ***2,5-g-B-3B*** = ***2,5-g-B-4A*** = ***2,5-g-B-4B*** = 1.19; ***2,5-g-B-5*** = 1.39; ***2,5-g-B-5'*** = 0.88; ***2,5-g-B-6A*** = ***2,5-g-B-6B*** = 1.19; ***2,5-g-B-7*** = 0.87. We consider these values as "estimated" ones for the spectral parameters of ***2,5-g-B-i***. Therefore, when discussing the results will use them gently, mainly to confirm some dependencies which are detected for the symmetrical 2,5-dimethylhexane **2,5-f** parameters.

The ***BSP*** values of six methyl protons (three H-1 and three H-2') in both 2,5-dimethylalkanes **2,5-n**, as in the case of 2-monomethylalkanes **2n**, are approximately equal to 0.870 ppm. However, for the 2,5-dimethylheptane **2,5-g** the authors of [2] are proposed a different (but very close) assignment (0.88ppm). For all these base parameters the calculated "standard" and "additional" differential parameters (***2,5-f-1*** = ***2,5-f-6***; ***2,5-f'-1*** = ***2,5-f'-6***; ***2,5-g-1***;***2,5-g-5'***; ***2,5-g-7***; ***2,5-g'-1***; ***2,5-g'-5'***; ***2,5-g'-7***) fall within the range of values from 0 to -10 **mlrd.**, or in the "strip" of "insufficiently valid" values. Therefore, it can be assumed that the introduction of additional methyl group to the C-5 carbon atom in chain of 2-methylalkane has virtually no effect (or only slightly affected) on the discussed methyl protons BSP values.

The ***BSP*** values of multiplet methine proton signal H-2 in both 2,5-dimethylalkanes **2,5-n** spectra, shown in [2], are different. The figure of ***2,5-f-B-2*** = ***2,5-f-B-5*** = 1.48 ppm of symmetrical 2.5-dimethylhexane **2,5-f** seems to be more correct. The figure of ***2,5-g-B-2*** = ***2,5-g-B-5*** = 1.39 ppm of 2.5-dimethylheptane **2,5-g** [2] (remember, it is one of only four for figures in the whole spectrum!) seems less plausible. The reason is that, since it is the same as for H-2 and H-5, which seems doubtful in the light of the findings for monomethylalkanes [1]. It can be assumed that this figure is an average value between the ***BSP*** values of low-field multiplet signals of the proton H-2(e.g., ***2,5-g-B-2*** ≈ 1.50 ppm) and more highfield value [e.g., ***2,5-g-B-5*** ≈ 1.30 ppm] of proton H-5 signal. The latter figure corresponds to approximately ***BSP*** values of methine protons H-3 in the 3-monomethylalkanes **3n** [1], which are the objects for comparison with ***BSP*** values doublet signal of the proton H-5 in 2.5-dimethylheptane **2,5-g**.

It is possible that the introduction of additional methyl group to the 5-C atom results in a small highfield shift (≈30 **mlrd.**) of the proton multiplet signal of H-2 ***BSP*** in 2,5-dimethylalkanes **2,5-n** (for example, to a value ***2,5-B-2*** ≈ $\boldsymbol{\delta^{H,mean.2,5\text{-}Me}_2 \approx 1.48 - 1.49}$**ppm**) compared to the ***BSP*** values of proton doublet signal of H-2 (***2-B-2*** ≈ $\boldsymbol{\delta^{H,ycp.2\text{-}Me}_2 = 1.520}$ **ppm**) in 2-(mono)methylalkanes **2n**. Due to the lack of reliable spectral data for a family of 2,5-dimethylalkanes **2,5-n** to make a more reliable conclusion is difficult.

As stated above, in 2,5-dimethylalkanes **2,5-n** two mentioned "tetracarbonic fragments "touchs each other" by two methylene groups $C^3H^3_2$ and $C^4H^4_2$ unlike similar fragments for 2,6-dimethylalkanes **2,6-n** which are separated with methylene group $C^4H^4_2$. Therefore, it is difficult to predict the mutual influence each other of these "tetracarbonic fragments" in 2,5-dimethylalkanes **2,5-n**. Besides, spectral parameters given in [2] (especially in the case of 2.5-dimethylheptane **2,5-g**), does not seem quite reliable because the methylene protons H-3 and H-4 therein, according to [2] are magnetically equivalent. The ***BSP*** values of these protons in the 2.5-dimethylhexane **2,5-f** pair wise equal and differ only slightly (30 **mlrd.**) from each other: upfield ***2,5-f-B-3A*** = ***2,5-f-B-4A*** = 1.14 ppm, and the downfield ***2,5-f-B-3B*** = ***2,5-f-B-4B*** = 1.17 ppm. The values of so called "aggregated" differential "standard" parameters ***2,5-f-3*** = ***2,5-f-4*** = **-115mlrd.** are in agreement very well with the similar value ***2n-3*** **= -110mlrd.** of 2-methylalkanes **2n**. The "additional" ("aggregated" parameters) ***DSP'***: ***2,5-f'-3*** = ***2,5-f'-4*** = **-115 – (-110)** **= -5mlrd.** expected close to zero.

As stated above, the "rounded" spectral parameters of 2.5-dimethylheptane **2,5-g** (***2,5-g-B-3A*** = ***2,5-g-B-3B*** = ***2,5-g-B-4A*** = ***2,5-g-B-4B*** = 1.19 ppm), we believe less valuable. Nevertheless, the "standard» ***DSP*** ("aggregated" parameters ***2,5-g-3*** = ***2,5-g-4*** = **-80mlrd.**) have the same sign and fairly close in value to corresponding parameters ***2n-3*** **= -110mlrd.** of **2-**methylalkanes **2n**.

Although, in fact, the estimative nature of the ***BSP*** values of methylene groups $C^3H^3_2$ protons in both 2,5-dimethylalkanes **2,5-f** and **2,5-g** (and methylene groups $C^4H^4_2$ protons in symmetrical 2.5-dimethylhexane **2,5-f**) we can do the cautious conclusion. It seems likely that the introduction of additional methyl group to the C-5 atom in the 2-methylalkanes **2n** only slightly changes (or does not change at all) the value of these protons ***BSP***. That is, both of interest **"tetracarbonic fragment**$\boldsymbol{[\text{-}C^{i\text{-}1}H^{i\text{-}1}_2\text{-}C^{i}H^{i}\ (C^{i'}H^{i'}_3)\text{–}C^{i+1}H^{i+1}_2\text{-}]}$(where n = 2 and 5) **substantially do not affect each other**.

3. 1. 3. The family of 2,4-dimethylalkanes 2,4-n.

In the spectra of 2,4-dimethylalkanes **2,4-n** of the general formula: $C^1H^1_3$-$C^2H^2(C^{2'}H^{2'}_3)$-$C^3H^3_2$-$C^4H^4(C^{4'}H^{4'}_3)$-$C^5H^5_2$-$C^6H^6_2$-...-$C^{\omega-1}H^{\omega-1}_2$-$C^{\omega}H^{\omega}_3$ both "tetracarbonic fragment" we are interested in **superimposed on one another**, so far as **they have a common methylene group –$C^3H^3_2$-**. Therefore, for the family of 2,4-dimethylalkanes **2,4-n** we can expected the mutual influence of two closely spaced methyl groups (at C-2 and C-4) on the ***BSP*** values of studied in this section molecule fragment C-1 –C-6, especially on the protons H-3.

Table 2 shows the protons ***BSP*** data only for three 2,4-dimethylalkanes **2,4-n** founded in the sources used [2,3]: symmetrical 2,4-dimethylpentane **2,4-e** [2,3], and asymmetrical 2,4-dimethylhexane **2,4-f** and 2,4-dimethylheptane **2,4-g** [3].

Table 2

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

Number of compound	Formula	The ***BSP*** values («$\delta^{H,\mathbf{2,4\text{-}n}}_i$») in ppm of specified number of "***i***-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.											
		3H 3x[H-1] (d)	1H [H-2] (m)	3H 3x[H-2'] (d)	1H [H-3A] (m)	1H [H-3B] (m)	1H [H-4] (m)	3H [H-4'] (d)	1H [H-5A] (m)	1H [H-5B] (m)	1H 1x[H-6A] (m)	1H 1x[H-6B] (m)	3H 3x[H-ω] (t)
2,4-e	$C^1H^1_3$-$C^2H^2(C^{2'}H^{2'}_3)$-$C^3H^3_2$-$C^4H^4_2(C^{4'}H^{4'}_3)$-$C^5H^5_3$	0.85 (0.853)	1.62 (1.619)	0.85 (0.853)	1.03 (1.028)	1.03 (1.028)	1.62 (1.619)	0.85 (0.853)					0.85 (0.853)
2,4-f	$C^1H^1_3$-$C^2H^2(C^{2'}H^{2'}_3)$-$C^3H^3_2$-$C^4H^4(C^{4'}H^{4'}_3)$-$C^5H^5_2$-$C^6H^6_3$	(0.840)	(1.63)	(0.866)	(0.97)	(1.11)	(1.38)	(0.827)	(1.11)	(1.31)			(0.858)
2,4-g	$C^1H^1_3$-$C^2H^2(C^{2'}H^{2'}_3)$-$C^3H^3_2$-$C^4H^4(C^{4'}H^{4'}_3)$-$C^5H^5_2$-$C^6H^6_2$-$C^7H^7_3$	(0.84)	(1.64)	(0.86)	(0.97)	(1.08)	(1.46)	(0.82)	(1.06)	(1.23)	(1.26)	(1.33)	(0.857)

In the spectrum of symmetrical 2,4-dimethylpentane **2,4-e** the BSP value of six methyl protons (three H-1 and three H-2') are equal to ***2,4-e-B-1*** = ***2,4-e-B-2'*** = 0.850 ppm (0.853 ppm). The "standard" and "additional" differential parameters are respectively: ***2,4-e-1*= -30mlrd.**; ***2,4-e'-1*= -15mlrd.**

In the spectra of the asymmetrical 2,4-dimethylhexane **2,4-f** and 2,4-dimethylheptane **2,4-g** the protons of methyl groups $C^1H^1_3$ and $C^{2'}H^{2'}_3$ are magnetically nonequivalent. The ***BSP*** values of three highfield methyl protons (labeled as H-1) are ***2,4-f-B-1*** = ***2,4-g-B-1***= 0.840 ppm. The ***BSP*** values of three lowfield methyl protons (labeled as H-2') are ***2,4-f-B-2'*** = 0.866 ppm, and ***2,4-g-B-2'***= 0.86 ppm. The difference between the magnitudes of highfield protons ***BSP*** values and lowfield protons ***BSP*** values of the methyl groups in these two 2.4-dimethylalkanes is about **20 ÷25mlrd.** The "standard" and "additional" differential parameters of 2.4dimethylhexane **2,4-f** are respectively: ***2,4-f-1*= -40mlrd.**; ***2,4-f'-1*= -25mlrd.**; ***2,4-f-2'*= -14mlrd.**; ***2,4-f'-2'*= +1mlrd.** For 2,4-dimethylheptane **2,4-g** these parameters are equal: ***2,4-g-1*= -40mlrd.**; ***2,4-g'-1*= -25mlrd.**; ***2,4-g-2'*= -20mlrd.**; ***2,4-g'-2'*= -5mlrd.**

In comparison with the corresponding average parameters of the 2-methylalkanes **2n** family (as well as with the parameters of the six magnetically equivalent protons in the 2,4-dimethylpentane **2,4-e**) let us calculate the **arithmetic mean value of the parameter** for the six protons H-1 and H-2' in the asymmetric 2,4-dimethylhexane **2,4-f** and 2,4-dimethylheptane **2,4-g**. Let us denote these parameters using two strokes after Latin letters denoting alkyl chain length (with ***i*** = 1) as: the parameter as "***2,4-n''-B-1***", the "standard" differential parameter as "***2,4-n''-1***", then the "additional" differential parameter will contain three strokes: "***2,4-n'''-1***". The calculated arithmetic mean value of these parameters are equal: for 2,4-dimethylhexane **2,4-f**: ***2,4-f''-B-1*** = 0.853 ррм; ***2,4-f''-1*** **= -27mlrd.**; ***2,4-f'''-1*= -12mlrd.**. For 2,4-dimethylheptane **2,4-g**: ***2,4-g''-B-1*** = 0.850 ррм; ***2,4-g''-1*** **= -30mlrd.**; ***2,4-g'''-1*=-15mlrd.**. A comparison with the corresponding parameters of 2,4-dimethylpentane **2,4-e** shows an almost complete identity for all three substances. That is, the ***average value*** of the two ***signals magnetically nonequivalent methyl group*** protons in the asymmetrical 2,4-dimethylalkanes **2,4-n** is substantially **equal** to the ***signal of magnetically equivalent protons*** in a symmetrical compound 2,4-dimethylpentane **2,4-e**.

Therefore, let us comment on the results of comparison the parameters of 2,4-dimethylpentane **2,4-e** (***2,4-e-1*= -30mlrd.**; ***2,4-e'-1*= -15mlrd.**),as a typical representative of the 2,4-dimethylalkanes **2,4-n** family with those of 2-methylalkanes family **2n** differential parameters (***2n-1*** **= -15mlrd.**). It can be considered to be established that the introduction of an additional methyl group to the C-4 atom, resulting in a significant (**-15mlrd.**) upfield shift of the each threeprotonic doublet signals of protons H-1 and H-2' in 2,4-dimethylalkanes **2,4-n**. This **upfield shift** can be interpreted as the **influence** of the **hydrogen atom H-4 replacement for methyl group** (**–$C^{4'}H^{4'}$**).

The ***BSP*** values of methine proton H-2 multiplet signal in all three spectra of 2,4-dimethylalkanes **2,4-n** fall in a narrow range from 1.62 to 1.64 ppm, the average value of ***2,4-n-B-2*** **= 1.630** ppm. The «standard» (***2,4-n-2*** = **+360mlrd.**) and "additional" (***2,4-n'-2*** = **+110mlrd.**) differential parameters have a **very large positive values**. A large value of the "additional" parameter indicates extra downfield shift of methine proton H-2 ***BSP*** values. It appears that a methyl group at C-4 is located close enough to protons H-1, H-2 and H-2' (through only one methylene group $C^3H^3_2$), and **so may have a marked effect on their *BSP*** values. It is possible that the **extra upfield shift of the *BSP* of three highfield protons H-1 doublet signal is compensated fairly significant by downfield shift of a single proton H-2 signal.**

The both protons of the methylene groups $C^3H^3_2$ multiplet signals are magnetically equivalent in the spectrum of symmetrical 2,4-dimethylpentane **2,4-e** (***2,4-e-B-3*** = 1.030 ppm) and magnetically nonequivalent in spectra of unsymmetrical 2,4-dimethylhexane **2,4-f** (***2,4-f-B-3A***= 0.970 ppм, ***2,4-f-B-3B*** = 1.110 ppм. The "aggregated" parameter ***2,4-f-B-3*** **=** 1.035 ppm) and for 2,4-dimethylheptane **2,4-g** (***2,4-g-B-3A*** = 0.970 ppм, ***2,4-g-B-3B*** = 1.070 ppм. The "aggregated" parameter ***2,4-g-B-3*** **=** 1.020 ppm). The arithmetic mean value of the basic parameter ***2,4-n-B-3*** = 1.030 ppm. The "standard" differential parameter (***2,4-n-3*** = **-240mlrd.**) has a very large negative value. It is logical to assume that the two protons H-3, which are located between the two "dicarbonic" fragments **-$C^iH^i(C^{i'}H^{i'}_3)$**, (where ***i*** = 2 and 4), subject to their simultaneous action. Let us suppose that both of these effects are independent and equal, according to [1], their action is determined by the sum of two "standard" differential parameters: the parameter ***2n-3*** **= -110mlrd.** of the fragment of **-$C^2H^2(C^{2'}H^{2'}_3)$** and the parameter ***4n-3*** **= -115mlrd.** of the fragment of **-$C^4H^4(C^{4'}H^{4'}_3)$**. Then their total impact is expected to equal **= -225mlrd.** Extra differential parameter (***2,4-n'-3***) we calculate as the difference between "standard" differential parameter (***2,4-n-3*** = **-240 mlrd.**) and the expected total calculated parameter (= **-225mlrd.**): ***2,4-n'-3*** = (-240) – (-225) = **-15 mlrd.**

It can be assumed that, by analogy with the existence of large positive "additional" differential parameter ***2,4-n'-2*** a small negative" additional" differential parameter ***2,4-n'-3*** is also exist (as in the case of a parameter ***2,4-n'-1***). All of these spectral changes (three "additional" differential parameters ***2,4-n'-1***, ***2,4-n'-2*** and ***2,4-n'-3***) can be regarded as a **result of perturbation of molecule arising in 2,4-dimethylalkanes 2,4-n as the reason of the introduction of additional methyl group to the C-4 atom (in place of the hydrogen atom H-4) in mono-2-methylalkane molecule**. Therefore, it may be appropriate to consider in the 2,4-, 3,5-, 4,6-, etc. families of the dimethylalkanes **N^1N^2-n** just the **"heptacarbonic" fragment** ***$[-C^{i-1}H^{i-1}_2-C^iH^i(C^{i'}H^{i'}_3)-C^{i+1}H^{i+1}_2-C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}_3)-C^{i+3}H^{i+3}_2-]$*** (as a whole moiety) as moiety that forming the spectral changes from the spectrum of the linear alkane. The test of this prediction performed by treating 3,5-dimethylalkanes **3,5-n**.

Let us consider the second part of the foresaid "heptacarbonic fragment", namely "tricarbonic fragment" **$[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_2-]$**, as well as additional methylene group **$–C^6H^6_2-$** in "long-chain" 2,4-dimethylalkanes **2,4-n**. The spectra signals of this fragment would be properly considered in other sections. Thus, for the 2.4-dimethylhexane **2,4-f** this piece is better viewed in section of 3,5-dimethylalkanes **3,5-n**, considering the molecule in reverse numbering of the carbon atoms of the molecule chain as a of 3,5-dimethylhexane **3,5-f** (see below). For similarly reason, 2.4-dimethylheptane **2,4-g** should be considered in Section 4,6-dimethylheptane **4,6-g**. But as the spectra signals of the "tricarbonic fragment" **$[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_2-]$**, in both these compounds (**2,4-f** and**2,4-g**) are very close in value, so we decide to review them here.

In the spectra of asymmetrical 2.4-dimethylhexane **2,4-f** (in reverse numbering "3,5-dimethylhexane" **3,5-f**), and 2.4-dimethylheptane **2,4-g** (in reverse numbering 4,6-dimethylheptane **4,6-g**) the doublet signal of the three protons of the methyl groups $C^{i'}H^{i'}_3$(***i*** =3 or 4) are fall in the range of ***2,4-f-B-3'*** ≈ ***2,3-g-B-4'*** from 0.820 ppm up to 0.827 ppm. The "standard" and "additional" differential arithmetic mean parameters computed for these compounds are, respectively: ***2,4-n-4'*** **= -55mlrd.**; ***2,4-n'-4'*** **= -40 mlrd.**

The arithmetic mean value of the basic parameter ***2,4-n-4'*** in asymmetrical 2,4-dimethylalkanes **2,4-n** is equal: ***2,4-n-4'*** **= -55mlrd.** It means, that three protons H-4 of methyl groups $C^{4'}H^{4'}_3$ in asymmetrical 2,4-

dimethylalkanes **2,4-n** absorb in a stronger field (approximately **-15 ÷ -20mlrd.**) than the similar protons in 4-monomethylalkanes **4n** (***4n-4’*= -40mlrd.**) and 5-monomethylalkanes **5n** (***5n-5’*= -35mlrd.**). Therefore, an additional upfield shift of the absorption of three protons H-4' in 2,4-dimethylalkanes **2,4-n** can be interpreted as **the result of the action of the hydrogen atom H-4 replacement on methyl group** in mono-2-methylalkanes **2n**.

The ***BSP*** values of multiplet signal of H-4 proton in the spectra of both asymmetrical (in reverse numbering "3,5-dimethylhexane” **3,5-f**) i.e., **2,4-f** (***2,4-f-B-4*** = 1.38 ppм, ***2,4-f-4*** = +110**mlrd.**), and ("4,6-dimethylheptane **4,6-g**”) **2,4-g** (***2,4-g-B-4*** = 1.46 ppm, ***2,4-g-4*** = +190**mlrd.**) substantially differ from each other, and the more different from a data of symmetrical 2,4-dimethylpentane **2,4-e** (***2,4-e-B-4*** = 1.62 ppm, ***2,4-e-4*** = +350**mlrd.**). This is not surprising, since they represent the different families of 2,N-dimethylalkanes.

Let us compare the"standard" differential parameter of reversely numbered "3.5-dimethylhexane **3,5-f”** i.e., **2,4-f** (***2,4-f-4*** = +110**mlrd.**) with previously defined [1] "standard" arithmetic mean value of the differential parameters of mono-3-methylalkanes ***3n-3* = +65mlrd.** Both parameters have a positive sign and a commensurate value. The "additional "differential” parameter calculated from their difference is ***2,4-f’-4*** = **+45mlrd.** On the other hand let’s compare the "standard" differential parameter of reversely numbered "4,6-dimethylheptane **4,6-g**” i.e., **2,4-g** (***2,4-g-4*** = +190**mlrd.**) with previously defined [1] "standard" arithmetic mean value of the differential parameter of mono-4-methylalkanes ***4n-4*= +115mlrd.** Here, both parameters are positive and comparable in magnitude. The "additional" differential parameter calculated from their difference (***2,4-g’-4*** = **+75mlrd.**)is quite a significant value.

In respect that the above calculated "additional" differential parameter (***2,4-e’-2*** = **+100mlrd.**) one can make the following conclusion. The significant value of the discussed "additional" parameter **indicates extra downfield shift** of considered methine proton H-4 ***BSP*** values in **2,4-f** (i.e., H-3 in the reversely numbered "3.5-dimethylhexane **3,5-f**); and ***BSP*** values of H-4 in the reverse numbered "4,6-dimethylheptane **4,6-g** (i.e., in **2,4-g**). Probably, the methyl group, situated at the β-carbon atom C-2 (i.e., through one methylene group $C^3H^3_2$) is located in the space close enough to the considered methine proton H-4, **and therefore causes a significant additional downfield shift of the considered multiplet signal of H-4 protons**. Perhaps this is offset to some extent compensated by offset discussed above upfield triprotonic doublet signal of H-4' in $C^4H^{4'}_3$ (approximately **-15 ÷ -20mlrd.** for each of the three protons).

The multiplet signals of both α-methylene groups protons ($C^2H^2_2$ by reverse numbering of “**3,5-f**” and $C^3H^3_2$ in “**4,6-g**”) in spectra of unsymmetrical 2,4-dimethylalkanes **2,4-f** and **2,4-g** are magnetically nonequivalent (***2,4-f-B-5A*** = 1.110 ppм, ***2,4-f-B-5B***= 1.310 ppм, the “aggregate” parameter of ***2,4-f-B-5* = 1.210 ppм**), and (***2,4-g-B-5A*** = 1.060 ppм, ***2,4-g-B-5B*** = 1.230ppm, the “aggregate” parameter ***2,4-g-B-5* = 1.145ppм**). The "standard"“aggregate” differential parameters ***2,4-f-5*** = **-60mlrd.** and ***2,4-g-5*** = **-125mlrd.** are negative, but differ significantly in size. Despite the fact that in this "reverse numbering" both compounds are from the different families of 2,N-dimethylalkanes their"additional"differential parameters ***2,4-f’-5*** = [(-60) – (-35)] = **-25mlrd.** and ***2,4-g’-5*** = [(-125) - (-115)] = **-10mlrd.** are close to zero value and both have a negative sign.

The multiplet signals of the two β-protons of the methylene group $C^6H^6_2$in the spectrum of asymmetrical 2.4-dimethylheptane **2,4-g** (designated in reverse numbering as"4,6-dimethylheptane **4,6-g**") are also magnetically nonequivalent (***2,4-g-B-6A*** = 1.260 ppм, ***2,4-g-B-6B*** = 1.330 ppm, the “aggregate” parameter ***2,4-g-B-6* = 1.295ppм**). The "standard" “aggregate” differential parameter ***2,4-g-6*** = **+25mlrd.** has a small absolute value and a positive sign, as compared parameters ***4n-6*** = **+ 25mlrd.** of mono-4-methylalkanes **4n**. The "additional "differential parameter ***2,4-g’-6*** = [(+25) - (+25)] = **0** coincides with the compared one of mono-4-methylalkanes **4n**. So we conclude that the **introduction of the methyl group** $C^{2'}H^{2'}_3$ at C-2 (instead of H-2) in 4-methylheptane **4g** has practically no effect on the absorption of β-protons H-6 of the methylene group $C^6H^6_2$ (***2,4-g’-6*= 0**).

3. 1. 4. The family of 2,3-dimethylalkanes2,3-n.

In the spectra of 2,3-dimethylalkanes **2,3-n** of the general formula: $C^1H^1_3$-$C^2H^2(C^{2'}H^{2'}_3)$-$C^3H^3(C^{3'}H^{3'}_3)$-$C^4H^4_2$-…-$C^{\omega-1}H^{\omega-1}_2$-$C^{\omega}H^{\omega}_3$ both " tetracarbonic fragment" we are interested are **superimposed on one another**, more precisely overlapping each other, whereby a methylene group is absent between them. Therefore, it may be appropriate to consider in the 2,3-, 3,4-, 4,5-, etc. families (as a whole moiety) of the dimethylalkanes just the **"hexacarbonic" fragment** $[-C^{i-1}H^{i-1}_{2}-C^{i}H^{i}(C^{i'}H^{i'}_{3})–C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}_{3})–C^{i+2}H^{i+2}_{2}-]$, as the moiety that forming the spectral changes from the spectrum of the linear alkane. The test of this prediction performed below by treating 3,4-dimethylalkanes **3,4-n** and 4,5-dimethylalkanes **4,5-n**.

That is, in the case of 2,3-dimethylalkanes **2,3-n** (for n = 2) one should considers the chemical shifts just the **"hexacarbonic"** integral moiety $[C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})–C^{4}H^{4}_{2}-]$, and further, the methylene group $–C^{5}H^{5}_{2}$-in along chain2,3-dimethylalkanes **2,3-n**.

Table 3 shows the proton ***BSP*** data of five compounds from the family of 2,3-dimethylalkanes **2,3-n** namely, symmetrical 2,3-dimethylbutane **2,3-d**, and unsymmetrical 2,3-dimethylpentane **2,3-e**, 2,3-dimethylhexane **2,3-f**, 2,3-dimethylheptane **2,3-g** and 2,3-dimethyloctane **2,3-h**. The spectra of the compounds **2,3-d** and **2,3-e** simultaneously are given in [2], and [3], while the spectra of the compounds **2,3-f**, **2,3-g** and **2,3-h** only in [2].

Table 3

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

Number of compound	Formula	The (*BSP*) values («$\delta^{H,2,3\text{-}n}_{i}$») in ppm of specified number of "*i*-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.									
		3H 3x[H-1] (d)	1H [H-2] (m)	3H 3x[H-2'] (d)	1H [H-3] (m)	3H [H-3'] (d)	1H [H-4A] (m)	1H [H-4B] (m)	1H [H-5A] (m)	1H [H-5B] (m)	3H 3x[H-ω] (t)
2,3-d	$C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})-C^{3}H^{3}-(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{3}$	0.84 (0.843)	1.41 (1.39)	0.84 (0.843)	1.41 (1.39)	0.84 (0.843)					0.84 (0.843)
2,3-e	$C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})-C^{3}H^{3}-(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-C^{5}H^{5}_{3}$	0.80 (0.796)	1.56 (1.56)	0.86 (0.856)	1.17 (1.17)	0.79 (0.788)	1.11 (1.10)	1.36 (1.36)			0.86 (0.863)
2,3-f	$C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})-C^{3}H^{3}-(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-C^{5}H^{5}_{2}-C^{6}H^{6}_{3}$	(0.798)	(1.54)	(0.853)	(1.35)	(0.781)	(1.06)	(1.22)	(1.28)	(1.28)	0.883
2,3-g	$C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})-C^{3}H^{3}-(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-C^{5}H^{5}_{2}-C^{6}H^{6}_{2}-C^{7}H^{7}_{3}$	(0.797)	(1.548)	(0.854)	(1.26)	(0.787)	(1.08)	(1.32)	(1.19)	(1.31)	0.892
2,3-h	$C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})-C^{3}H^{3}-(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-C^{5}H^{5}_{2}-C^{6}H^{6}_{2}-C^{7}H^{7}_{2}-C^{8}H^{8}_{3}$	(0.796)	(1.54)	(0.853)	(1.27)	(0.786)	(1.07)	(1.30)	(1.28)	(1.28)	0.887

Let us consider the spectrum of a symmetrical shortchain 2,3-dimethylbutane **2,3-d**, then the spectrum of an asymmetrical midchain 2,3-dimethylpentane **2,3-e**, jointly the spectra of three asymmetrical "true longchain" 2.3-dimethylalkanes **2,3-f, 2,3-g** and **2,3-h**. Below we show that the last four spectrum are useful to view together, and it is for them to calculate the arithmetic mean parameters.

The spectrum of symmetric shortchain 2,3-dimethylbutane **2,3-d**. The ***BSP*** value of twelve methyl protons (three H-1, three H-2 ', three H-3' and three H-4) are equal to ***2,3-d-B-1*** = ***2,3-d-B-2'*** = ***2,3-d-B-3'*** = ***2,3-d-B-2'*** = 0.840 ppm (0.843 ppm). The "standard" and "additional" differential parameters are, respectively: ***2,4-d-1*** = **-40mlrd.**; ***2,4-d'-1*** = **-25mlrd.** Two methine proton (H-2 and H-3) ***BSP*** value are equal to ***2,3-d-B-2*** = ***2,3-d-B-3*** = 1.41 ppm (the "standard" and "additional" differential parameters are, respectively: ***2,4-d-1***= **+140mlrd.**; ***2,4-d'-1***= **-110mlrd.**). As shown below, due to the absence of the carbon chain attached to the atom C-4 in 2,3-dimethylbutane **2,3-d**, these parameters are fundamentally different from the arithmetic mean values of the parameters characteristic of the longchain 2.3-dimethylalkanes.

In the spectra of asymmetrical midchain 2,3-dimethylpentane **2,3-e** and "truly longchain" 2,3-dimethylalkanes **2,3-f - 2,3-h** the six protons of the two methyl groups $C^{1}H^{1}_{3}$ and $C^{2'}H^{2'}_{3}$ are magnetically nonequivalent. The ***BSP*** value of highfield three methyl protons (designated as H-1) are in a very narrow range of ***2,3-e-B-1*** ≈ ***2,3-f-B-1***≈ ***2,3-g-B-1*** ≈ ***2,3-h-B-1*** from 0.796 ppm up to 0.798 ppm. The ***BSP*** value of lowfield three methyl protons (labeled as H-2') are in a somewhat wider range of values ***2,3-e-B-2'*** ≈ ***2,3-f-B-2'*** ≈ ***2,3-g-B-2'*** ≈ ***2,3-h-B-2'*** from 0.853 ppm to 0.86 ppm. The downfield interval boundary is due to the midchain 2,3-dimethylpentane **2,3-e** ***BSP*** value: **2,3-e**: ***2,3-e-B-2'*** = 0.856 [2]; ***2,3-e-B-2'*** = 0.86 [3]. Note that for the "truly longchain" 2,3-dimethylalkanes **2,3-f - 2,3-h** the interval is narrower: from 0.853 ppm up to 0.854 ppm. The "standard" and the "additional" arithmetic mean values of the differential parameters calculated for all 4 longchain 2,3-dimethylalkanes **2,3-f - 2,3-h** are respectively: for highfield methyl groups ***2,3-n-1*= -85mlrd.**; ***2,3-n'-1*= -70mlrd.** For lowfield methyl groups: ***2,3-n-2'*= -45mlrd.**; ***2,3-n'-2'*= -30mlrd.** There is observed a significantly larger difference (about **60 mlrd.**) between highfield ***BSP*** value (***2,3-n-B-1*** = 0.795 ppm) and lowfield one (***2,3-n-B-2'*** = 0.855 ppm) of the methyl groups in 2,3-dimethylalkanes **2,3-n** on the one hand and the values of ***2,4-n-B-2'*** = 0.865ppм and ***2,4-n-B-1***= 0.840 ppm in 2,4 - dimethylalkanes **2,4-n** on the other (the difference is **25 mlrd.**).

For comparison with arithmetic mean values of the family of 2-methylalkanes **2n** parameters (as well as with parameters and twelve magnetic equivalent protons in 2,3-dimethylbutane **2,3-d**), by analogy with the above described 2,4- dimethylalkanes let us calculate the **arithmetic mean values of six protons H-1 and H-2' parameters** for four asymmetric 2,3-dimethylalkanes **2,3-e - 2,3-h**: the basic parameter ***2,3-n''-B-1*** = **0.825 ppm**; the "standard" differential parameter ***2,3-n''-1* = -55mlrd.**; and the "additional" differential parameter ***2,3-n'''-1* = -40mlrd.** Comparison with the above parameters of 2,3-dimethylbutane **2,3-d** show a significant upfield shift of arithmetic mean of six proton H-1 and H-2' parameters in asymmetrical 2,3-dimethylalkanes **2,3-e - 2,3-h**. That is, the **average signal of two magnetically nonequivalent methyl groups** in the asymmetric 2,3-dimethylalkanes absorbs **in highly field** than the **magnetic equivalent protons** in a symmetric shortchain 2,3-dimethylbutane **2,3-d**, and in extra stronger field, than absorption in mono-2-methylalkanes **2n**. Such extra highfield shift of six protons H-1 and H-2' absorption in all five 2,3-dimethylalkanes **2,3-d - 2,3-h** can be interpreted as **the result of action of hydrogen atom H-3 replacement on methyl group** in mono-2- methylalkanes.

In the spectra of asymmetrical longchain 2,3-dimethylalkanes: the midchain 2,3-dimethylpentane **2,3-e** and "truly longchain" 2,3-dimethylalkanes **2,3-f - 2,3-h** the methine groupC^2H^2 proton H-2 absorption ***BSP*** parameters (***2,3-e-B-2* ≈ *2,3-f-B-2* ≈ *2,3-g-B-2* ≈ *2,3-h-B-2***) are in a narrow range from1.540 ppm up to 1.56 ppm. The downfield interval boundary is due to just the midchain 2,3-dimethylpentane **2,3-e *BSP*** value: ***2,3-e-B-2*** = 1.56 ppm [2,3]. Note that for the "truly longchain" 2,3-dimethylalkanes **2,3-f - 2,3-h** the interval is narrower, from 1.54 ppm to 1.55 ppm. The "standard" and the "additional" arithmetic mean values of the differential parameters calculated for all 4 longchain 2,3-dimethylalkanes **2,3-e - 2,3-h** are respectively: ***2,3-n-2*= +280mlrd.**; ***2,3-n'-2'*= +30mlrd.** 2,3-dimethylbutane **2,3-d** we consider not as linear but as branched alkane, therefore the value of ***2,3-d-B-2*** = 1.40 ppm in it differs significantly from the above-considered parameter ***2,3-n-B-2*** = 1.55 ppm.

It can be concluded that due to disturbance occurring in molecules of mono-2-methylalkanes during the introduction of a methyl group to the atom C-3 (instead of the hydrogen atomH-3), a marked upfield proton shift of signals H-1 and H-2' in the resulting 2,3-dimethylalkanes [sum parameter mutation] is: ***2,3-n-1*** and ***2,3-n-2'***: 6 x(-40) = **-240mlrd.** This mutation to some extent compensated by downfield shift of methine H-2 proton signal:[1 x (+30) = +30 mlrd.].

Let us consider the second part of the foresaid "hexacarbonic fragment", namely "tricarbonic fragment" **$[-C^3H^3(C^{3'}H^{3'}{}_3)–C^4H^4{}_2-]$**, as well as additional methylene group **$–C^5H^5{}_2-$** in "long-chain" 2,3-dimethylalkanes **2,3-n**. As in the case of 2,4-dimethylalkanes, the signals of the fragment would be properly considered in other sections. Thus, for the 2,3-dimethylpentane **2,3-e** this piece is better viewed in section of 3,4-dimethylalkanes **3,4-n**, considering the molecule in reverse numbering of the carbon atoms of the molecule chain as a of 3,4-dimethylpentane **3,4-e** (see below). For similarly reason, 2,3-dimethylhexane **2,3-f** will be considered as 4,5-dimethylhexane **4,5-f**; 2,3-dimethylheptane **2,3-g** will be considered as 4,5-dimethylheptane **5,6-g** and 2,3-dimethyloktane **2,3-h** - as 6,7-dimethyloktane **6,7-h**. But as the spectra signals of the "tricarbonic fragment" **$[-C^3H^3(C^{3'}H^{3'}{}_3)–C^4H^4{}_2-]$** in all these compounds (**2,3-e -2,3-h**) are very close in value, so we decide to review them here.

In the spectra of asymmetrical midchain 2,3-dimethylpentane **2,3-e** and "truly longchain" 2.3-dimethylalkanes **2,3-f - 2,3-h** the doublet signals of three protons of the methyl group $C^{3'}H^{3'}{}_3$ (***2,3-e-B-3'* ≈ *2,3-f-B-3'* ≈ *2,3-g-B-3'* ≈ *2,3-h-B-3'***) are in the narrow range of from 0.781 ppm up to 0.790 ppm (the downfield interval boundary is due to just the midchain 2,3-dimethylpentane **2,3-e *BSP*** value: ***2,3-e-B-3'*** = 0.790 ppm [2]; ***2,3-e-B-3'*** = 0.788 ppm [3]. Note that for the "truly longchain" 2,3-dimethylalkanes **2,3-f - 2,3-h** the interval is narrower: from 0.781 ppm up to 0.787 ppm. The "standard" and the "additional" arithmetic mean values of the differential parameters calculated for all 4 longchain 2,3-dimethylalkanes **2,3-f - 2,3-h** are respectively: ***2,3-n-3'*= -95mlrd.**; ***2,3-n'-3'*= -80mlrd.**

The signal $C^{3'}H^{3'}{}_3$ methyl group in the asymmetrical 2,3-dimethylalkanes **2,3-n** (the «standard» parameter ***2,3-n-3'*= -95mlrd.**). is detected in a much more highfield (***2,3-n'-3'* ≈ -60mlrd.**), than similar averaged signals in different monomethylalkane families: **3n** (***3n-3'*= -35 mlrd.**), **4n** (***4n-4'*= -40 mlrd.**)

and **5n** (***5n-5'*= -35mlrd.**). It can be assumed that the parameters of protons ***6n-6'*** in the family of 6,7-dimethylalkanes (including of interest here reverse numbered "6,7-dimethyloctane **6,7-h**", i.e., 2,3-dimethyloctane **2,3-h**) would also be approximately equal to **35-40 mlrd.** Therefore, an extra upfield shift of three protons H-3' absorption in 2,3-dimethylalkanes (***2,3-n'-3'*** **≈-60mlrd.**) can be interpreted as **the result of action of hydrogen atom H-3 replacement on methyl group** in mono-2- methylalkanes.

In the spectra of asymmetrical midchain 2,3-dimethylpentane **2,3-e** and "truly longchain" 2.3-dimethylalkanes **2,3-f - 2,3-h** the multiplet signals of methine proton $C^{3}H^{3}$ [the ***BSP*** values: ***2,3-e-B-3*** = 1.17 (1.17); ***2,3-f-B-3*** = (1.35); ***2,3-g-B-3*** = (1.27); ***2,3-h-B-3*** = (1.26) are given in ppm] are in a very wide range of values from 1.17 ppm to 1.35 ppm. For midchain 2,3-dimethylpentane **2,3-e** is found the most upfield shift of the signal. For "truly longchain" 2.3-dimethylalkanes **2,3-f - 2,3-h** the interval was narrower, from 1.26 ppm to 1.35 ppm. We have no explanation for such a large range of parameters studied. Nevertheless, let us calculate the arithmetic mean values of basic parameter (***2,3-n-B-3'*** = 1.265 ppm). The arithmetic mean values of the "standard" and the "additional" differential parameters calculated for all 4 longchain 2,3-dimethylalkanes **2,3-f - 2,3-h**, are respectively equal to: ***2,3-n-3*= -10mlrd.**; ***2,3-n'-3'*= -75mlrd.** However, these parameters do not seem sufficiently reliable.

The multiplet signals of both α-methylene protons $C^{4}H^{4}_{2}$ ($C^{n-1}H^{n-1}_{2}$ by reverse numbering of asymmetrical 2,3-dimethylalkanes **2,3-e - 2,3-h**) are magnetically nonequivalent (***2,3-e-B-4A*** = 1.110 ppm, ***2,3-e-B-4B*** = 1.360 ppm, the " aggregated" parameter ***2,3-e-B-4*** **= 1.230 ppm**; ***2,3-f-B-4A*** = 1.060 ppm, ***2,3-f-B-4B*** = 1.220 ppm, the " aggregated" parameter ***2,3-f-B-4*** **= 1.140 ppm**; ***2,3-g-B-4A*** = 1.080 ppm, ***2,3-g-B-4B*** = 1.320 ppm, the " aggregated" parameter ***2,3-g-B-4*** **= 1.20 ppm**; ***2,3-h-B-4A*** = 1.070 ppm, ***2,3-h-B-4B*** = 1.300 ppm, the " aggregated" parameter ***2,3-h-B-4*** **= 1.185ppm**). The "standard" "aggregated" parameter are equal to ***2,3-e-4*** **= -40mlrd.**, ***2,3-f-4*** **= -130mlrd.**, ***2,3-g-4*** **= -70mlrd.**, ***2,3-h-4*** **= -85mlrd.**, and all are negative, but differ significantly in values. As in the case of 2,4-dimethylalkanes **2,4-n** spite of the fact that in this "reverse numeration" all 4 compounds represent different families of dimethylalkanes, their "additional" differential parameters are close to zero magnitude and have a negative sign: ***2,3-e'-4*** = [(-40) – (-35)] = **-5mlrd.**; ***2,3-f'-4*** = [(-130) – (-115)] = **-15mlrd.** and ***2,3-g'-4***=[(-110) - (-100)] = **-10mlrd.** Let us assume the" additional" differential parameter ***2,3-n'-4*** for the whole 2,3-dimethylalkanes **2,3-e** family equal to ***2,3-n'-4*= -10mlrd.**

The multiplet signals of both β-protons of the methylene group $C^{5}H^{5}_{2}$ ($C^{3}H^{3}_{2}$ by reverse numbering in 5,6-dimethylheptane **5,6-g**) in the spectrum of an asymmetrical 2,3-dimethylheptane **2,3-g,** as the abovementioned α-protons $C^{4}H^{4}_{2}$, are magnetically nonequivalent(***2,3-g-B-5A*** = 1.190 ppm, ***2,3-g-B-5B*** = 1.310 ppm, the " aggregated" parameter ***2,3-g-B-5*** **= 1.250** ppm). Both the proton H-5 in the remaining two 2,3-dimethylalkanes **2,3-f** and **2,3-h** are magnetically equivalent and absorb at 1.28 ppm (***2,3-f-B-5*** = ***2,3-h-B-5*** = 1.280 ppm). The values of all three discussed basic parameters (***2,3-f-B-5***, ***2,3-g-B-5*** and ***2,3-h-B-5***) fall into the "strip of insufficiently validity values" (i.e., in the range from 1.25 ppm up to 1.29 ppm).

So we conclude that **the introduction of methyl group** instead of hydrogen atom H-2 at C-2 in longchain mono-3-methylalkanes **3n** to form the 2,3-dimethylalkanes **2,3-n does not influence the absorption** of **proton of β–methylene group** $C^{5}H^{5}_{2}$ (i.e. which is located in the β -position relative to C-3).

3. 1. 5. The family of 2,2-dimethylalkanes 2,2-n.

In the spectra of 2,2-dimethylalkanes **2,2-n** of the general formula: $C^{1}H^{1}_{3}$-$C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})$-$C^{3}H^{3}_{2}$-$C^{4}H^{4}_{2}$-…-$C^{\omega-1}H^{\omega-1}_{2}$-$C^{\omega}H^{\omega}_{3}$ both "tetracarbonic fragment" we are interested **[-$C^{i-1}H^{i-1}_{2}$-$C^{i}H^{i}(C^{i'}H^{i'}_{3})$–$C^{i+1}H^{i+1}_{2}$-]** ($i$ = 2)are **completely overlap each other**, whereby new, not before seen a tricarbonic fragment [-$C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})$-] is formed. Therefore, it may be appropriate to consider in the spectra of 2,2-dimethylalkanes **2,2-n** families ***as a whole moiety*** just the **"pentacarbonic" fragment** *[$C^{1}H^{1}_{3}$-$C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})$–$C^{3}H^{3}_{2}$-],* as the **moiety that forming the spectral changes** from the spectrum of the linear alkane, as well as an additional methylene group **–$C^{4}H^{4}_{2}$-** in longchain 2,2-dimethylalkanes **2,2-n**.

Table 4 shows the proton ***BSP*** data of five compounds from the family of 2,2-dimethylalkanes **2,2-n** namely, symmetrical 2,2-dimethylpropane **2,2-c** and unsymmetrical 2,2-dimethylbutane **2,2-d**, 2,2-dimethylpentane **2,2-e**, 2,2-dimethylhexane **2,2-f** and 2,2-dimethyloctane **2,2-h**. The spectra of the compounds **2,2-d**, **2,3-e** and **2,2-f** simultaneously are given in [2], and [3], while the spectra of the compounds **2,2-c** and **2,2-h** only in [2].

Table 4

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

Number of compound	Formula	The (***BSP***) values («$\delta^{H,2,2\text{-}n}_{i}$») in ppm of specified number of "***i***-type" protons denoted in brackets. In parenthesis below is shown the signal multiplicity.								
		3H 3x[H-1] (s)	3H 3x[H-2'] (s)	3H 3[H-2''] (s)	1H [H-3A] (m)	3H [H-3B] (m)	1H [H-4A] (m)	1H [H-4B] (m)	2H 2x[H-ω-1] (m)	3H 3x[H-ω] (t)
2,2-c	$(C^{1}H^{1}_{3})C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{-}C^{3}H^{3}_{3}$	(0.902, CCl_4)	(0.902, CCl_4)	(0.902, CCl_4)						(0.902, CCl_4)
2,2-d	$(C^{1}H^{1}_{3})C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{3}$	0.86 (0.855)	0.86 (0.855)	0.86 (0.855)	1.215 (1.22)	1.215 (1.22)				0.820 (0.840)
2,2-e	$(C^{1}H^{1}_{3})C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{3}\text{-}C^{5}H^{5}_{3}$	0.86 (0.864)	0.86 (0.864)	0.86 (0.864)	1.15??? (1.18)	1.15??? (1.18)			1.25??? (1.18)	0.880 (0.880)
2,2-f	$(C^{1}H^{1}_{3})C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{3}\text{-}C^{5}H^{5}_{3}$	0.86 (0.865)	0.86 (0.865)	0.86 (0.865)	1.10-130 (1.23)	1.10-130 (1.23)	1.10-130 (1.17)	1.10-130 (1.17)	1.10-130 (1.28)	0.900 (0.900)
2,2-h	$(C^{1}H^{1}_{3})C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{3}\text{-}C^{5}H^{5}_{2}\text{-}C^{3}H^{3}_{2}\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	(0.863)	(0.863)	(0.863)	(1.16)	(1.16)	(1.25)	(1.25)	(1.30)	0.900 (0.900)

The spectral data of following 2,2-dimethylalkanes **2,2-n**: **2,2-d**, **2,2-h** and possibly, **2,2-f** we submitted as the most reliable. In the spectrum of 2,2-dimethylpentane **2,2-e**, given in [2], the methylene protons H-3 and H-4 ***BSP*** values are equal to each other (***2,2-e-B-3*** = ***2,2-e-B-4*** = 1.18 ppm), which is in doubt. Our interpretation of the compounds **2,2-e** and **2,2-f** spectra, described in [3], is not reliably grounded, so in Table 4 either is an interval (as for **2,2-f**),or a particularly questionable figures, accompanied by three question marks (as for **2,2-e**)

The spectrum of 2,2-dimethylpropane **2,2-c** is obtained in carbon tetrachloride [2] and is given merely as illustrative material, and therefore it will not be discussed. Due to the lack of carbon chain length beginning from C-4 (single atom C-4) in unsymmetrical 2,2-dimethylbutane **2,2-d**, the compound **2,2-d** (as well as **2,2-c**), we believe as the branched alkanes and not as linear ones and therefore we believe the protons ***BSP*** value in them are not typical for a family of 2,2-dimethylalkanes **2,2-n**.

Let us consider the spectra of "atypical" shortchain 2,2-dimethylbutane **2,2-d**, then the spectra of the "typical", midchain 2,2-dimethylpentane **2,2-e** and then the spectra of two "truly longchain" 2,2-dimethylalkanes **2,2-f** and **2,2-h**. Below we show that the last three spectrum are useful to viewed together, and it is for them to calculate the arithmetic mean parameters.

The absorption of nine magnetically equivalent methyl protons (three H-1, three H-2'and three H-2'') of the four 2,2-dimethylalkanes: **2,2-d, 2,2-e, 2,2-f** and **2,2-h** is shown in the singlet signal of 9H intensity. Their ***BSP*** values are from 0.855 to 0.865 ppm, and the upfield interval boundary is due to just the shortchain 2,2-dimethylbutane **2,2-d**: ***2,2-d-B-1*** = ***2,2-d-B-2'*** = ***2,2-d-B-2''*** = 0.86 ppm [3],0.855ppm [2]. Note that for the "truly longchain" 2,2-dimethylalkanes **2,2-e, 2,2-f** and **2,2-h** the interval is narrower: from 0.863 ppm up to 0.865 ppm. The "standard" and "additional" differential arithmetic mean parameters calculated for 2,2-dimethylalkanes **2,2-d - 2,2-h** are respectively equal: ***2,2-n-1***= **-20mlrd.**; ***2,2-n'-1***= **-5mlrd.** The introduced to the existing one methyl substituent at carbon atom C-2 in mono-2-methylalkanes the second methyl groups $C^{2''}H^{2''}_{3}$ (instead of the second hydrogen atom H-2) has only a very small (almost zero) impact on the formed nonaprotonic singlet signal of methyl protons H-1, H-2 'and H-2'' ***BSP*** value, shifting it insignificantly further upfield (***2,2-n'-1***= **-5mlrd.**).

The methine protons in 2,2-dimethylalkanes **2,2-d - 2,2-h** are absent.

The methylene protons of $C^{3}H^{3}_{2}$ groups. Despite the fact that in the spectrum of shortchain 2,2-dimethylbutane **2,2-d** the ***BSP*** value (***2,2-d-B-3*** = 1.220 ppm, ***2,2-d-3*** = **-50mlrd.**) is reliably established, this parameter is not regarded as informative, since because too short carbon chain molecule protons H-3 exposed so called "end effects influence".

The α-methylene groups $C^{3}H^{3}_{2}$ protons in other 2,2-dimethylalkanes **2,2-e - 2,2-h** accordingly to the authors[2] data are magnetically equivalent, but in the spectra of longchain 2,2-dimethylalkanes **2,2-n** they give hard interpreted multiplet signals. In the spectra of 2,2-dimethylpentane **2,2-e** as described above, the signals $C^3H^3_2$ methylene group assignment is not reliable, so that data will not be discussed. The author [2] assignmentof the methylene groups $C^3H^3_2$ and $C^4H^4_2$ proton signals of 2,2-dimethylhexane **2,2-f** (cf.the attribution of the same signals in the 2,2-dimethyloctane **2,2-h**) appears doubtful. It seems more likely the opposite assignment: ***2,2-f-B-3*** = 1.170 ppm and ***2,2-f-B-4*** = 1.230 ppm. Only for 2,2-dimethyloctane **2,2-h** the author [2] assignment of signals (***2,2-h-B-3*** = 1.160 ppm and ***2,2-h-B-4*** = 1.250 ppm), as the attribution of other methylene groups $C^5H^5_2$, $C^6H^6_2$ and $C^7H^7_2$ protons signals seems correct. The "standard" and the "additional" differential arithmetic mean parameters values calculated for 3 longchain 2,2-dimehyilalkanes **2,2-e; 2,2-f** and **2,2-h** are respectively equal: ***2,2-n-3*= -100mlrd.**; ***2,2-n'-3*= +10mlrd.**

The β-protons of the methylene groups $C^4H^4_2$ signals in the spectra of longchain 2,2-dimethylalkanes **2,2-n** [except 2,2-dimethyloctane **2,2-h** (***2,2-h-B-4*** = 1.250 ppm, ***2,2-h-4*= -20mlrd.**; ***2,2-h'-3*= -10mlrd.**)] are interpreted in our opinion not reliable (see above attribution signals 2,2-dimethylhexane **2,2-f**).The parameters β-methylene protons values of 2,2-dimethyloctane **2,2-h** were approximately equal to the arithmetic mean differential parameters ***2n-4* =-10 mlrd.** in 2-methylalkanes **2n**; but both of these parameters fall into the "strip of insufficiently validity values" (i.e., in the range from 1.25 ppm up to 1.29 ppm).

Therefore it is possible to formulate the following cautious conclusion. Simultaneous introduction of two methyl groups instead of two hydrogen atoms at carbonC-2 of ethyl moiety converts the C-1 - C-2 dicarbonic fragment into substituted tert-butyl group. The ***BSP*** values of methylene groups $\mathbf{C^3H^3_2}$ and $\mathbf{C^4H^4_2}$ protons, which are subsequent to this "substituted tert-butyl moiety", are uniquely shifted upfield, but this shifts are approximately equal the same ones occurring when to the carbon atom C-2 of unsubstituted alkanes is introduced the only one methyl group, i.e., the conversion to mono-2-methylalkanes.

3. 2. The Families of 3,N-dimethylalkanes 3,N-n.

To calculate the family of 3,N-dimethylalkanes **"additional"** values of ***DSP'***, let us bring to mind the arithmetic mean parameters of the "standard" ***DSP*** (***3n-i***, expressed in **mlrd.**),which were calculated for a family of mono-3-methylalkanes **3n** [1]:]: ***3n-1* = -25**; ***3n-2* =-35**; ***3n-3* = +65**; ***3n-4* =-105**; ***3n-ω*= + 5** and ***3n-3'*= -35**.

The NMR ^{1}H spectra of 3,N-dimethylalkanes which are available to us and contain the most "remote" second methyl group (at $\mathbf{N^2}$ = 7), were considered first. Then, as in the case 2,N-dimethylalkanes **2,N-n**, gradually, "bringing closer" a second methyl group to first one we reach to the "vic-location" in the 3,4-dimethylalkanes **3,4-n** and finally to the "gem-location" in the 3,3-dimethylalkanes **3,3-n**.

3. 2. 1. The family of 3,7-dimethylalkanes 3,7-n.

The only representative of a 3,7-dimethylalkanes **3,7-n**, NMR spectra of which is given in the sources we use [2,3], is the above-considered 2,6-dimethyloctane **2,6-h**, indicated by reverse numbering as "3,7-dimethyloctane **3,7-h**». In the reverse numbering of the carbon atoms of the alkyl chain of **2,6-h** the methyl group at C-2 (in direct numbering), becomes the methyl group at C-7 (in reverse numbering), and the methyl group at C-6 (in direct numbering), becomes the methyl group at C-3 (in reverse numbering).

Previously, we considered the first part of its spectrum, i.e., the fragment comprising C-1 – C-4. Now let us consider the second part of its spectrum, i.e. fragment C-5 - C-8 (denoted in reverse numbering as C-1 – C-4). The values of the base (***3,7-h-B-i***) and "standard" differential (***3,7-h-i***) parameters (in reverse numbering), indicated in 3,7-dimethyloctane **3,7-h** (i = 1 ÷ 4) are listed below in **reverse numbering**: ***3,7-h-B-1*** = 0.857 ppm, ***3,7-h-1*** = -23**mlrd.**; ***3,7-h-B-2A*** = 1.15ppm, ***3,7-h-2A*** = -120**mlrd.**; ***3,7-h-B-2B*** = 1.34 ppm, ***3,7-h-2B*** = +70**mlrd.**, ***3,7-h-2*** = -25**mlrd.**; ***3,7-h-B-3*** = 1.29 ppm, ***3,7-h-3*** = +20**mlrd.**; ***3,7-h-B-3'*** = 0.846 ppm, ***3,7-h-3'*** = -34**mlrd.**; ***3,7-h-B-4A*** = 1.08ppm, ***3,7-h-4A*** = -190 **mlrd.**; ***3,7-h-B-4B*** = 1.26 ppm, ***3,7-h-4B*** = -10**mlrd.**, ***3,7-h-4*** = -100**mlrd.**

To calculate the "additional" differential parameters ***3,7-h'-I*** (the following in reverse numbering) let us use as subtrahend the arithmetic mean parameters of the "standard" ***DSP 3n-i***, expressed in **mlrd.**: ***3,7-h'-1*** = [(-23) – (-25)] = **+2mlrd.**; ***3,7-h'-2*** = [(-25) – (-35)] = **+10mlrd.**; ***3,7-h'-3*** = [(+20) – (+65)] = **-45mlrd.**; ***3,7-h'-3'*** = [(-34) – (-35)] = **+1mlrd.**; ***3,7-h'-4*** = [(-100) – (-105)] = **+5mlrd.** Except for the parameter ***3,7-h'-3*** (**-45mlrd.**) all other the "additional" differential parameters ***3,7-h'-I*** does not exceed by the absolute value of **10 mlrd.**, and therefore fall into the "strip of insufficiently validity values", i.e. in fact, are" zero". Therefore, given in mind the "unreliability attribution" of polyprotonic multiplet signals of range 1.0 -1.4 ppm, which includes the present authors [2] the ***BSP*** methine proton value ***3,7-h-B-3*** = 1.29 ppm, the value of "additional" differential parameter ***3,7-h'-3*** = **-45mlrd.** appears debatable.

Given this, we can conclude that the introduction of second methyl groups instead of hydrogen atoms at carbon C-7along with the existing methyl groups at carbon C-3 (to form the 3,7-dimethylalkanes **3,7-n** by reverse numbering) **as expected, almost no effect on the absorption of the fragment C-1 - C-4** (by reverse numbering) **protons**.

3. 2. 2. The family of 3,6-dimethylalkanes <u>3,6-n</u>.

Unfortunately, we use sources [2,3] there is no credible spectral data given for the sole representative of the family 3,6-dimethylalkanes **3,6-n** – the 3,6-dimethylheptane **3,6-g** (on the reverse numbering), i.e. for above-considered 2,5- dimethylheptane **2,5-g** (indirect numbering). Therefore, such a review is meaningless and will not be held.

3.2. 3. The family of 3,5-dimethylalkanes <u>3,5-n</u>.

The general formula of 3,5-dimethylalkanes **3,5-n** is as follows: $\mathbf{C^1H^1{}_3\text{-}C^2H^2{}_2\text{-}C^3H^3(C^{3'}H^{3'}{}_3)\text{-}C^4H^4{}_2\text{-}C^5H^5(C^{5'}H^{5'}{}_3)\text{-}C^6H^6{}_2\text{-}\ldots\text{-}C^{\omega-1}H^{\omega-1}{}_2\text{-}C^{\omega}H^{\omega}{}_3}$. Some of 2,4-dimethylalkanes **2,4-n** may be considered as 3,5-dimethylalkanes **3,5-n**, if reverse numbering of the alkyl chain carbon atoms. For example, it is 2,4-dimethyl hexane **2,4-f** (it named on the reverse numbering as 3,5-dimethylhexane **3,5-f**). Previously, we considered a part of the spectrum of 2,4-dimethylhexane **2,4-f**, a fragment comprising the C-1 - C-4 protons, when we are interested of the ***BSP*** value changing when introduced to a molecule of 2-methylhexane an additional methyl group at C-4. Now we consider a similar task to track the changes of protons H-5, H-5' and H-6 (reverse numbering) ***BSP*** value when introduced into molecule of 3-methylhexane an additional methyl group at C-5, i.e. consider the fragment $\mathbf{\text{-}C^5H^5(C^{5'}H^{5'}{}_3)\text{-}C^6H^6{}_3}$**.**

In 3,5-dimethylalkanes **3,5-n** (as in the examined above 2,4-dimethylalkanes **2,4-n**) both of interest "tetracarbonic fragments" $\mathbf{[\text{-}C^{i-1}H^{i-1}{}_2\text{-}C^iH^i(C^{i'}H^{i'}{}_3)\text{–}C^{i+1}H^{i+1}{}_2\text{-}]}$ superimposed on one another, with the mutual methylene group $\mathbf{\text{–}C^4H^4{}_2\text{-}}$**.** Therefore, they can expect a similar to "2,4-dimethylalkanes **2,4-n**" effect of two closely spaced methyl groups(at C-3 and C-5) on the ***BSP*** value of studied in this section part of the molecule C-1-C-6, especially on the protonsH-4.

In the sources we use [2,3], there are PMR spectra of three 3,5-dimethylalkanes **3,5-n** representatives. Besides the above-considered reverse numbered asymmetrical shortchain 3,5-dimethylhexane **3,5-f** (i.e. 2,4-dimethylhexane **2,4-f** in direct numbering), there are a "symmetrical" 3,5-dimethylheptane **3,5-g** and "asymmetrical" "truly longchain" 3,5-dimethyloctane **3,5-h**.

For the symmetrical 3,5-dimethylheptane **3,5-g** PMR spectrum the authors [2] led an unique attribution the proton signals. They identified two stereoisomers in spectrum and attribute every signal to each of these isomers protons. For the spectrum of 3,5-dimethyloctane **3,5-h** authors [2] referring of signals are not informative, so this spectrum will not be commented on.

<u>3,5-dimethylhexane 3,5-f (in reverse numbering).</u> The values of base ***3,5-f-B-I*** and the "standard" differential ***3,5-f-I*** parameters reversibly numbered 3,5-dimethylhexane **3,5-f** are following: ***3,5-f-B-1*** = 0.858 ppm, ***3,5-f -1*** = -22 **mlrd.**; ***3,5-f-B-2A*** = 1.11 ppm; ***3,5-f-2A*** = -160 **mlrd.**; ***3,5-f-B-2B*** = 1.31 ppm; ***3,5-f-2B*** = +40 **mlrd.**, ***3,5-f-2*** = -60 **mlrd.**; ***3,5-f-B-3*** = 1.38 ppm, ***3,5-f-3*** = +110 **mlrd.**; ***3,5-f-B-3'*** = 0.827 ppm, ***3,5-f-3'*** = -53 **mlrd.** The ***3,5-f-B-4*** and ***3,5-f-4*** parameters are accepted equal to ***2,4-f-B-3*** **=** 1.035 ppm and ***2,5-f-3*** = -235 **mlrd.**, which are previously discussed (see above). Let us calculate the "additional" differential parameters ***3,5-f'-I*** according to the above formula parameter ***3,5-f'-1*** = [(-26) – (-25)] = **-1mlrd.**; ***3,5-f'-2*** = [(-55) – (-35)] = **-20mlrd.**; ***3,5-f'-3*** = [(+120) – (+65)] = **+55mlrd.**; ***3,5-f'-3'*** = [(-62) – (-35)] = **-27mlrd.**; ***3,5-f'-4*** = ***2,4-f'-3*** = [(-235) – (-225)] = **-10mlrd.**

<u>3,5-dimethylheptane 3,5-g.</u>

<u>The first isomer of symmetrical ***3,5-dimethylheptane*** **3,5-g1**</u>. The values of base ***3,5-g1-B-i*** and the "standard" differential ***3,5-g1-I*** parameters of the first isomer of the symmetrical 3,5-dimethylheptane **3,5-g** designated as **3,5-g1**, are the following: : ***3,5-g1-B-1*** = 0.854 ppm, ***3,5-g1-1*** = - 26 **mlrd.**; ***3,5-g1-B-2A*** = 1.08 ppm, ***3,5-g1-2A*** = -190 **mlrd.**; ***3,5-g1-B-2B*** = 1.35 ppm, ***3,5-g1-2B*** = +80 **mlrd.**, ***3,5-g1-2*** = -55 **mlrd.**; ***3,5-g1-B-3*** = 1.39 ppm, ***3,5-g1-3*** = +120 **mlrd.**; ***3,5-g1-B-3'*** = 0.818ppm, ***3,5-g1-3'*** = -62 **mlrd.**; ***3,5-g1-B-4*** = 1.05 ppm, ***3,5-g1-4*** = -220 **mlrd.**

<u>The second isomer of symmetrical ***3,5-dimethylheptane*** **3,5-g2**</u>. The values of base ***3,5-g2-B-i*** and the "standard" differential ***3,5-g2-I*** parameters of second isomer of the symmetrical 3,5-dimethylheptane

3,5-gdesignated as **3,5-g2**, are the following: ***3,5-g2-B-1*** = 0.864 ppm, ***3,5-g2-1*** = -16 **mlrd.**; ***3,5-g2-B-2A*** = 1.14ppm, ***3,5-g2-2A***= -130 **mlrd.**; ***3,5-g2-B-2B*** = 1.28ppm, ***3,5-g2-2B*** = +10 **mlrd.**, ***3,5-g2-2*** = -60**mlrd.**; ***3,5-g2-B-3*** = 1.41ppm, ***3,5-g2-3*** = +140 **mlrd.**; ***3,5-g2-B-3’*** = 0.836 ppm, ***3,5-g2-3’*** = -44**mlrd.**; ***3,5-g2-B-4*** =1.05 ppm, ***3,5-g2-4*** = -220 **mlrd.**

The "additional" differential parameters ***3,5-g’-I*** of the ***3,5-dimethylheptane*** (**3,5-g1** and **3,5-g2**).To calculate the "additional" differential parameters ***3,5-g’-I*** of the first and second isomers of 3,5-dimethylheptane **3,5-g** as subtrahend arithmetic means applies the above parameters of the "standard» ***DSP*** ***3n-i***. Then the parameters of the first isomer **3,5-g1** (***3,5-g1’-i***) are: ***3,5-g1’-1*** = [(-26) – (-25)] = **-1mlrd.**; ***3,5-g1’-2*** = [(-55) – (-35)] = **-20mlrd.**; ***3,5-g1’-3*** = [(+120) – (+65)] = **+55mlrd.**; ***3,5-g1’-3’***= [(-62) – (-35)] = **-27 mlrd.**; ***3,5-g1’-4***= [(-220) – (-105)] = **-115mlrd.** The "additional" differential parameters of the second isomer**3,5-g2** (***3,5-g2’-i***) are: ***3,5-g2’-1*** = [(-16) – (-25)] = **+9mlrd.**; ***3,5-g2’-2*** = [(-60) – (-35)] = **-25mlrd.**; ***3,5-g1’-3*** = [(+140) – (+65)] = **+75mlrd.**; ***3,5-g1’-3’*** = [(-44) – (-35)] = **-9mlrd.**; ***3,5-g1’-4***= [(-220) – (-225)] = **+5mlrd.**

The “aggregated”parameters of ***3,5-dimethylheptane 3,5-g***. Let us calculate the arithmetic mean values of the "standard" and the "additional" differential parameters for both isomers of 3,5-dimethylheptane **3,5-g** (3,5-g1+ 3,5-g2),as half the sum of the relevant parameters of both isomers. Let us denote these “aggregated” parameters as ”***3,5-g-I***” and “***3,5-g’-i***” and round it to the nearest multiple of 5number:

3,5-g-1 = [(-26) + (-16)]/2 ≈ -20 **mlrd.**; ***3,5-g’-1*** = [(-1) + (+9)]/2 ≈ **+5mlrd.**;
3,5-g-2 = [(-55) + (-60)]/2 ≈ -60**mlrd.**; ***3,5-g2’-2*** = [(-20) + (-25)] /2 ≈ **-25mlrd.**;
3,5-g-3 = [(+120) + (+140)]/2 = **+130mlrd.**; ***3,5-g1’-3*** = [(+55) + (+75)] /2 = **+65mlrd.**;
3,5-g-3’ = [(-62) + (-44)]/2 ≈ **-55mlrd.**; ***3,5-g1’-3’*** = [(-27) + (-9)] /2 ≈ **-20mlrd.**;
3,5-g-4 = [(-220) + (-220)]/2 = **-220mlrd.**; ***3,5-g1’-4*** = [(-220) + (-225)] /2 = **+5mlrd.**

The arithmetic mean values of all the parameters of the family 3,5-dimethylalkanes **3,5-n**. Let us calculate the arithmetic mean values of the "standard" ***3,5-n-I*** and the "additional" ***3,5-n’-I*** differential parameters for spectra of two 3,5-dimethylalkanes **3,5-n**: **3,5-f** and **3,5-g** (rounding parameters values of 3,5-dimethylhexane **3,5-f**),and take them as **parameters of the whole family of 3,5-dimethylalkanes 3,5-n:**

3,5-n-1 = [(-20) + (-20)]/2 = **-20mlrd.**; ***3,5-n’-1*** = [(0) + (+5)]/2 = **+5mlrd.**;
3,5-n-2 = [(-60) + (-60)]/2 = **-60mlrd.**; ***3,5-n’-2*** = [(-20) + (-25)]/2 = **-25 mlrd.**;
3,5-n-3 = [(+110) + (+130)]/2 = **+120mlrd.**; ***3,5-n’-3*** = [(+55) + (+65)]/2 ≈ **+60mlrd.**;
3,5-n-3’= [(-55) + (-55)]/2 = **-55mlrd.**; ***3,5-n’- 3’*** = [(-25) + (-20)]/2 ≈ **-25mlrd.**;
3,5-n-4 = [(-235) + (-220)]/2 = **-230mlrd.** ***3,5-n’-4*** = [(-10) + (+5)]/2 = **-5mlrd.**

Let us compare the arithmetic mean values of the "standard" and the "additional" differential parameters of heptacarbonic fragment$[-C^{i-1}H^{i-1}_{2}-C^{i}H^{i}(C^{i'}H^{i'}_{3})-C^{i+1}H^{i+1}_{2}-C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}_{3})-C^{i+3}H^{i+3}_{2}-]$, where ***i*** = 3, obtained for the family of 3,5-dimethylalkanes **3,5-n**, with the same parameters in the same heptacarbonic fragment obtained for the family of 2,4-dimethylalkanes **2,4-n**, wherein ***i*** = 2. The comparison advisable to carry out of a **tricarbonic fragment** $[-C^{i+1}H^{i+1}_{2}-C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}_{3})-]$, i.e., in the same part of above heptacarbonic fragment, wherein the effects of terminal fragments vicinity are minimized in both families of compared dimethylalkanes **2,4-n** and **3,5-n**. For the case of the family of 3,5-dimethylalkanes **3,5-n** the fragment $[-C^{4}H^{4}_{2}-C^{5}H^{5}(C^{5'}H^{5'}_{3})-]$ coincides with the already discussed fragment $[-C^{3}H^{3}(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-]$. For the case of a family of dimethylalkanes **2,4-n** this section will be: $[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})-]$. Let us compared mentioned values expressed in **mlrd.**

2,4-n-3* = -240** versus ***3,5-n-4 = -230 ***2,4-n’-3* = -15** versus ***3,5-n’-4* = -5**
2,4-n-4* = +150** versus ***3,5-n-4 = +120 ***2,4-n’-4* = +35** versus ***3,5-n’-5* = +60**
***2,4-n- 4’* = -55** versus ***3,5-n- 5’* = -55** ***2,4-n’-4’* = -40** versus ***3,5-n’- 3’* = -40**

From the above comparison table one can see very good agreement in magnitude and sign of the corresponding "standard" and "additional" differential parameters, except for the parameters characterizing the methine protons H-4 in 2,4-dimethylalkanes **2,4-n** and H-5 in 3,5-dimethylalkanes **3,5-n**. To explain this discrepancy we must remember about that it has been repeatedly said before about the "unreliability of assignments" of the protons entering the polyprotonic multiplet signal in the range of 1.0 - 1.5 ppm. Therefore, we can conclude that the second methyl group is introduced to an C-5 atom in mono-3-methylalkanes (i.e. in linear alkanes already having a methyl substituent at C-3) as expected, will have almost the same effect on the protons absorption of considered pentacarbonic fragment in the resulting

3,5-dimethylalkanes **3,5-n**, what we previously observed in similar in structure the 2,4-dimethylalkanes **2,4-n** family.

3. 2. 4. The family of 3,4-dimethylalkanes 3,4-n.

In the spectra of 3,4-dimethylalkanes **3,4-n** of the general formula: $C^1H^1_3$-$C^2H^2_2$-$C^3H^3(C^{3'}H^{3'}_3)$-$C^4H^4(C^{4'}H^{4'}_3)$-$C^5H^5_2$-…-$C^{\omega-1}H^{\omega-1}_2$-$C^{\omega}H^{\omega}_3$ both "tetracarbonic fragment" we are interested are partially **superimposed on one another**, more precisely overlapping each other, whereby a methylene group is absent between them. Therefore, it may be appropriate to consider in the 3,4-dimethylalkanes **3,4-n** family (as a whole moiety) just the **"hexacarbonic" fragment** $[-C^{i-1}H^{i-1}_2-C^iH^i(C^{i'}H^{i'}_3)–C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}_3)–C^{i+2}H^{i+2}_2-]$, as moiety that forming the spectral changes from the spectrum of the linear alkane. That is, in the case of 3,4-dimethylalkanes **3,4-n** (for ***i*** = 3) one should considers the chemical shifts just the **"hexacarbonic"** integral moiety $[C^2H^2_2-C^3H^3(C^{3'}H^{3'}_3)–C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_2-]$, and further, the methylene group $–C^6H^6_2-$ in a longchain 3,4-dimethylalkanes **3,4-n**.

In the sources we use [2,3], there is PMR spectrum of the sole representatives of 3,4-dimethylalkanes **3,4-n** family – the symmetrical 3,4-dimethylhexane **3,4-f**. In its PMR spectrum the authors [2] led an unique attribution the proton signals. They identified two stereoisomers in spectrum and attribute every signal to each of these isomers protons. As the molecule 3,4-dimethylhexane **3,4-f** is symmetrical, for it is sufficient to consider only a fragment of the C-1 to C-3.

The first isomer of symmetrical ***3,4-dimethylhexane*** **3,4-f1**. The values of base ***3,4-f1-B-i*** and the "standard" differential ***3,4-f1-I*** parameters of the first isomer of the symmetrical 3,4-dimethylhexane **3,4-f** designated as **3,4-f1**, are the following: ***3,4-f1-B-1*** = 0.867ppm, ***3,4-f1-1*** = - 13 **mlrd.**; ***3,4-f1-B-2A*** = 1.070ppm, ***3,4-f1-2A*** = -200 **mlrd.**; ***3,4-f1-B-2B*** = 1.38ppm, ***3,4-f1-2B*** = +110 **mlrd.**, ***3,4-f1-B-2*** = 1.225 ppm, ***3,4-f1-2*** = -45 **mlrd.**; ***3,4-f1-B-3*** = 1.28ppm, ***3,4-f1-3*** = +10 **mlrd.**; ***3,4-f1-B-3'*** = 0.816 ppm, ***3,4-f1-3'*** = -64**mlrd.**

The second isomer of symmetrical ***3,4-dimethylhexane*** **3,4-f2**. The values of base ***3,4-f2-B-i*** and the "standard" differential ***3,4-f2-I*** parameters of second isomer of the symmetrical 3,4-dimethylhexane **3,4-f** designated as **3,4-f2**, are the following: : ***3,4-f2-B-1*** = 0.862 ppm, ***3,4-f2-1*** = -18 **mlrd.**; ***3,4-f2-B-2A*** = 1.16 ppm, ***3,4-f2-2A*** = -110 **mlrd.**; ***3,4-f2-B-2B*** = 1.32 ppm, ***3,4-f2-2B*** = +50 **mlrd.**; ***3,4-f2-B-2*** = 1.24 ppm, ***3,4-f2-2*** = -30 **mlrd.**; ***3,4-f2-B-3*** = 1.32 ppm,***3,4-f2-3*** = +50 **mlrd.**; ***3,4-f2-B-3'*** = 0.744 ppm, ***3,4 -f2-3'*** = -136**mlrd.**

The "additional" differential parameters ***3,4-f'-I*** of the ***3,4-dimethylhexane*** (**3,4-f1** and **3,4-f2**).To calculate the "additional" differential parameters ***3,4-f'-I*** of the first and second isomers of 3,4-dimethylheptane **3,4-f** as subtrahend arithmetic means applies the above parameters of the "standard» ***DSP 3n-i***. Then the parameters of the first isomer **3,4-f1** (***3,4-f1'-i***) are: ***3,4-f1'-1*** = [(-13) – (-25)] = **-12mlrd.**; ***3,4-f1'-2*** = [(-45) – (-35)] = **-10mlrd.**; ***3,4-f1'-3*** = [(+10) – (+65)] = **-55mlrd.**; ***3,4-f1'-3'***= [(-64) – (-35)] = **-29 mlrd.** The "additional" differential parameters of the second isomer **3,4-f2** (***3,4-f2'-i***) are: ***3,4-f2'-1***= [(-18) – (-25)] = **+7mlrd.**; ***3,4-f2'-2*** = [(-30) – (-35)] = **+5mlrd.**; ***3,4-f1'-3*** = [(+50) – (+65)] = **-15mlrd.**; ***3,4-f1'-3'*** = [(-136) – (-35)] = **-101mlrd.**

The "aggregated"**"standard" "*3,4-f-i*" and the "additional" "*3,4-f'-i*" differential parameters** for both isomers of ***3,4-dimethylhexane*** (**3,4-f1**and**3,4-f2**).Let us calculate these parameters as half the sum of the relevant parameters of both isomers and round it to the nearest multiple of 5number:

3,4-f-1 = [(-13) + (-18)]/2 ≈ -15 **mlrd.**; ***3,4-f'-1***= [(-12) + (+7)]/2 ≈ **-5mlrd.**;
3,4-f-2 = [(-45) + (-30)]/2 ≈ -40 **mlrd.**; ***3,4-f'-2*** = [(-10) + (+5)] /2 ≈ **-5mlrd.**;
3,4-f-3 = [(+10) + (+50)]/2 = **+30mlrd.**; ***3,4-f'-3*** = [(-55) + (-15)] /2 = **-35mlrd.**;
3,4-f-3' = [(-64) + (-136)]/2 ≈ **-100mlrd.**; ***3,4-f'-3'*** = [(-29) + (-101)] /2 ≈ **-65mlrd.**

Since the 3,4-dimethylalkanes **3,4-n** family shown in our study, only one compound - the symmetrical 3,4-dimethylhexane **3,4-f**, its calculated parameters "***3,4-f-i***" and "***3,4-f'-I***" take as arithmetic mean values of the "standard" ("***3,4-n-i***") and the "additional" ("***3,4-n'-i***") differential parameters of the whole 3,4-dimethylalkanes **3,4-n** family. Let us compare these parameters ***3,4-n-I*** and ***3,4-n'-I*** in the hexacarbonic fragment $[-C^{i-1}H^{i-1}_2-C^iH^i(C^{i'}H^{i'}_3)–C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}_3)–C^{i+2}H^{i+2}_2-]$, where ***i***=3, with the same parameters in the same hexacarbonic fragment obtained for the family of 2,3-dimethylalkanes **2,3-n**, wherein ***i*** =2. The comparison advisable to carry out of a tetracarbonic fragment $[-C^{i+1}H^{i+1}_2-C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}_3)-C^{i+3}H^{i+3}_2]$, i.e., in the same part above hexacarbonic fragment, wherein the effects of terminal fragments vicinity are minimized in both families of compared dimethylalkanes **2,3-n** and **3,4-n**. For the case of the symmetrical 3,4-dimethylhexane **3,4-f** the fragment $[-C^{4}H^{4}(C^{4'}H^{4'}_{3})-C^{5}H^{5}-]$ coincides with the already discussed fragment $[-C^{2}H^{2}_{2}-C^{3}H^{3}(C^{3'}H^{3'}_{3})-]$. For the case of a family o dimethylalkanes **2,3-n** this section will be: $[-C^{3}H^{3}(C^{3'}H^{3'}_{3})-C^{4}H^{4}-]$. Let us compared mentioned values expressed in **mlrd.**

***2,3-n-3*= -10** versus ***3,4-n'-3* = +30** ***2,3-n'-3*=-75** versus ***3,4-n'-3* = -35**

***2,3-n-3'*= -95** versus ***3,4-n'-3'* = -100** ***2,3-n'-3'*=+35** versus ***3,4-n'-3'* = +60**

***2,3-n- 4*= -80** versus ***3,4-n'- 2* =-40** ***2,3-n'-4*=-10** versus ***3,4-n'- 2* = -5**

From the above comparison table one can see quite satisfactory agreement in magnitude (the differences do not exceed|40 **mlrd.**|)of the corresponding "standard" and "additional" differential parameters, except for the parameters characterizing the methine protons H-3 in 2,3-dimethylalkanes **2,3-n** and H-4 in 3,4-dimethylhexane **3,4-f**. To explain this discrepancy we must remember about that it has been repeatedly said before about the "unreliability of assignments" of the protons entering the polyprotonic multiplet signal in the range of 1.0 - 1.5 ppm. Therefore, we can conclude that the second methyl group is introduced to an C-4 atom in mono-3-methylalkanes (i.e. in linear alkanes already having a methyl substituent at C-3) will have a **similar effect on the protons absorption of considered tricarbonic fragment** in the resulting 3,4dimethylalkanes **3,4-n**, what we previously observed in similar in structure the 2,3-dimethylalkanes **2,3-n** family.

3. 2. 5. The family of 3,3-dimethylalkanes 3,3-n.

In the spectra of 3,3-dimethylalkanes **3,3-n** family of the general formula: $C^{1}H^{1}_{3}-C^{2}H^{2}_{2}-C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})-C^{4}H^{4}_{2}-C^{5}H^{5}_{2}-\ldots-C^{\omega-1}H^{\omega-1}_{2}-C^{\omega}H^{\omega}_{3}$ both "tetracarbonic fragment" we are interested are **completely overlap one another**, forming a tricarbonic fragment $[-C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})-]$ a similar to fragment$[-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})-]$ in 2,2-dimethylalkanes **2,2-n**. Therefore, as in 2,2-dimethylalkanes **2,2-n** it may be appropriate to consider in the 3,3-dimethylalkanes **3,3-n** familiy just the **"pentacarbonic" fragment** $[C^{2}H^{2}_{2}-C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})-C^{4}H^{4}_{2}-]$, (as a whole moiety) as moiety that forming the spectral changes from the spectrum of the linear alkane; as well as an additional the methylene group $-C^{6}H^{6}_{2}-$ in a longchain 3,3-dimethylalkanes **3,3-n**.

In the sources we use [2,3], there are PMR spectra of two 3,3-dimethylalkanes **3,3-n** representatives: the symmetrical midchain 3,3-dimethylpentane **3,3-e** and "asymmetrical" "truly longchain"3,3-dimethyloctane **3,3-h**.

As the molecule 3,3-dimethylpentane **3,3-e** is symmetrical, for it is sufficient to consider only a fragment of the C-1 to C-3. The values of base ***3,3-e-B-i*** and the "standard" differential ***3,3-e-I*** parameters of the symmetrical 3,3-dimethylpentane **3,3-e** are the following: ***3,3-e-B-1*** = 0.790 ppm, ***3,3-e-1*** = -90**mlrd.**; ***3,3-e-B-2*** = 1.205 ppm, ***3,3-e-2*** = -65**mlrd.**; ***3,3-e-B-3'*** = 0.800 ppm, ***3,3-e-3'*** = -80**mlrd.**; ***3,3-e-B-3''*** = 0.800 ppm, ***3,3-e-3''***= -80 **mlrd.**

The molecule 3,3-dimethyloctane **3,3-h** is asymmetrical, and a longchain. Therefore, we consider the fragment of the molecule C-1 - C-5. The values of base ***3,3-h-B-i*** and the "standard" differential ***3,3-h-I*** parameters of the asymmetrical 3,3-dimethyloctane **3,3-h** are the following: ***3,3-h-B-1*** = 0.789 ppm, ***3,3-h-1*** = -91 **mlrd.**; ***3,3-h-B-2*** = 1.206 ppm, ***3,3-h-2*** = -64 **mlrd.**; ***3,3-h-B-3'*** = 0.806ppm, ***3,3-e-3'***= -74 **mlrd.**; ***3,3-h-B-3''*** = 0.806 ppm, ***3,3-h-3''***= -74 **mlrd.**; ***3,3-h-B-4***= 1.15 ppm, ***3,3-h-4***= -120 **mlrd.**; ***3,3-h-B-5***= 1.21 ppm, ***3,3-h-5***= -60**mlrd.** Let's give also the values of proton H-6, H-7 and H-8 chemical shifts, given in [2]: ***3,3-h-B-6*** = 1.21 ppm, ***3,3-h-B-7*** = 1.30 ppm, ***3,3-h-B-8*** = 0.886 ppm. If the values of the base parameters ***3,3-h-B-7*** and ***3,3-h-B-8*** is not in doubt, because they are expected for a longchain alkanes, the parameter values ***3,3-h-B-5*** and especially ***3,3-h-B-6***, in our opinion, does not correspond to the expected in the longchain alkanes. Therefore, the parameters of the protons H-5 will not be discussed.

The "additional" differential parameters ***3,3-e'-i*** values of the symmetrical 3,3-dimethylpentane **3,3-e** are the following: ***3,3-e'-1*** = [(-90) – (-25)] = **-65mlrd.**; ***3,3-e'-2*** = [(-65) – (-35)] = **-30mlrd.**; ***3,3-e'-3'*** = ***3,3-e'-3''*** = [(-80) – (-35)] = **-45mlrd.** The values of the "additional" differential parameters ***3,3-h'-i*** of the longchain 3,3-dimethyloctane **3,3-h** are the following: ***3,3-h'-1*** = [(-91) – (-25)] = **-66mlrd.**; ***3,3-h'-2*** = [(-64) – (-35)] = **-29mlrd.**; ***3,3-h'-3'*** = ***3,3-h'-3''*** = [(-74) – (-35)] = **-39mlrd.**; ***3,3-h'-4*** = [(-120) – (-105)] = **-15mlrd.**

Let's calculate the "standard" ***3,3-n-i*** and the "additional" ***3,3-n'-I*** rounded arithmetic mean values of the differential parameters calculated for these two 3,3-dimethylalkanes **3,3-n**: **3,3-e** and **3,3-h** and take them as arithmetic mean values ("***3,3-n-i*** ") and ("***3,3-n'-i***") of differential parameters of the whole 3,4-

dimethylalkanes **3,4-n**family: ***3,3-n-1* = -90mlrd.**, ***3,3-n'-1*= -65mlrd.**; ***3,3-n-2*= -65mlrd.**, ***3,3-n'-2* = -30mlrd.**; ***3,3-n-3'* = *3,3-n-3''* = -80mlrd.**, ***3,3-n'-3'* = *3,3-n'-3''* ≈ -45 mlrd.** The parameters ***3,3-n-4*** and ***3,3-n'-4*** meaningful only for the longchain alkanes, so they coincide with the largest parameter ***3,3-h-4* = -120 mlrd.** and ***3,3-h'-4* = -15mlrd.**

Let us compare of the analogous parameters for the family of 3,3-dimethylalkanes **3,3-n** and of 2,2-dimethylalkanes **2,2-n** family. The comparison advisable to carry out of such protons signals, wherein the effects of terminal fragments vicinity are minimized in both families of compared dimethylalkanes **2,2-n** and **3,3-n**.Therefore, it seems appropriate to compare only the two pairs of signals from the two protons underlined α-methylene groups.

1.For the case of shortchain compounds: a) 2,2-dimethylbutane **2,2-d** the fragment $C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}\underline{C^{3}H^{3}_{2}}\text{-}C^{4}H^{4}_{3}$ and b) for 3,3-dimethylpentane **3,3-f** the fragment $C^{1}H^{1}_{3}\text{-}\underline{C^{2}H^{2}_{2}}\text{-}C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})\text{–}\underline{C^{4}H^{4}_{2}}\text{-}C^{5}H^{5}_{3}$. Let's similize the comparable quantities expressed in mlrd.

***2,2-d-3* = -50mlrd.** versus ***3,3-e-2* = *3,3-e-4* = -65mlrd.** The difference is **|15 mlrd. |**

2.For the case of longchain asimmetricasl compounds: a) 2,2-dimethylalkanes (**2,2-e - 2,2-h**) of the general formula $C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}\underline{C^{3}H^{3}_{2}}\text{-}C^{4}H^{4}_{2}\text{-}\ldots\text{-}C^{\omega-1}H^{\omega-1}_{2}\text{-}C^{\omega}H^{\omega}_{3}$ and b) for 3,3-dimethyloctane **3,3-h** $C^{1}H^{1}_{3}\text{-}C^{2}H^{2}_{2}\text{-}C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})\text{–}\underline{C^{4}H^{4}_{2}}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$. Let's compare the parameter of the methylene group $\text{-}C^{4}H^{4}\text{-}$ in 3,3-dimethyloctane **3,3-h** with similar parameters of the methylene group $\text{-}C^{3}H^{3}\text{-}$ in longchain 2,2-dimethylalkanes (**2,2-e - 2,2-h**) expressed in mlrd.

***2,2-n-3* = -100mlrd.** versus ***3,3-h-4* = -120mlrd.** The difference is **|20 mlrd.|**

From the above comparison table one can see fairly good agreement in magnitude (the differences do not exceed|20**mlrd.**|)of the corresponding "standard" (and hence, the "additional") differential parameters. Therefore, we can conclude that the second methyl group is introduced to an C-3 atom in mono-3-methylalkanes (i.e. in linear alkanes already having a methyl substituent at C-3 leading to the formation of gem-compounds - 3,3-dimethylalkanees **3,3-n**) will have a **similar effect on the absorption** of underlined α-methylene groups **protons** ($\text{-}\underline{C^{4}H^{4}_{2}}\text{-}$), as the part of pentacarbonic **fragment** $[\text{-}C^{2}H^{2}_{2}\text{-}C^{3}(C^{3'}H^{3'}_{3})(C^{3''}H^{3''}_{3})\text{–}\underline{C^{4}H^{4}_{2}}\text{-}]$, as α-methylene groups ($\text{-}\underline{C^{3}H^{3}_{2}}\text{-}$) in fragment $[\text{-}C^{1}H^{1}_{2}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}\underline{C^{3}H^{3}_{2}\text{-}}]$in similar in structure the 2,2-dimethylalkanes **2,2-n** family.

3. 3. The Families of 4,N-dimethylalkanes 4,N-n.

To calculate the family of 4,N-dimethylalkanes **"additional"** values of ***DSP'***, let us bring to mind the arithmetic mean parameters of the "standard" ***DSP*** (*4n-i*, expressed in **mlrd.**), which were calculated for a family of mono-4-methylalkanes **4n** [1]:]: ***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**.

The NMR ^{1}H spectrum of 4,N-dimethylalkane which are available to us and contain the most "remote" second methyl group (at $\mathbf{N^{2}}$ = 6), is the spectrum of the above-considered 2,4-dimethylheptane **2,4-g** (indicated by reverse numbering as "4,6-dimethylheptane **4,6-g**"). Then, as in the case of N,N'-dimethylalkanes **N,N'-n**, gradually, "bringing closer" a second methyl group to first one (at C-4) we reach to the "gem-location" in the 4,4-dimethylalkanes **4,4-n**. In the sources used [2,3]because of the limited length of the alkyl chain NMR spectra are only two types of 4,N-dimethylalkanes - 4,5- and 4,4-dimethyloctanes.

3. 3. 1. The family of 4,5-dimethylalkanes 4,5-n.

In the spectra of 4,5-dimethylalkanes **4,5-n** of the general formula: $C^{1}H^{1}_{3}\text{-}C^{2}H^{2}_{2}\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{-}C^{5}H^{5}(C^{5'}H^{5'}_{3})\text{-}C^{6}H^{6}_{2}\text{-}\ldots\text{-}C^{\omega-1}H^{\omega-1}_{2}\text{-}C^{\omega}H^{\omega}_{3}$ both "tetracarbonic fragment" we are interested $[\text{-}[\text{-}C^{i-1}H^{i-1}_{2}\text{-}C^{i}H^{i}\ (C^{i'}H^{i'}_{3})\text{–}C^{i+1}H^{i+1}_{2}\text{-}]$ *i* = 4, 5) are partially **superimposed on one another**, more precisely overlapping each other, whereby a methylene group is absent between them. Therefore, in the 4,5-dimethylalkanes **4,5-n** family there is a whole moiety - just the **"hexacarbonic" fragment** $[\text{-}C^{i-1}H^{i-1}_{2}\text{-}C^{i}H^{i}(C^{i'}H^{i'}_{3})\text{–}C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}_{3})\text{–}C^{i+2}H^{i+2}_{2}\text{-}]$, as moiety that forming the spectral changes from the spectrum of the linear alkane. That is, in the case of 4,5-dimethylalkanes **4,5-n** (for n = 4) this fragment is $[C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{–}C^{5}H^{5}(C^{5'}H^{5'}_{3})\text{–}C^{6}H^{6}_{2}\text{-}]$. Next, we consider the methylene group $\text{–}C^{6}H^{6}_{2}\text{-}$ in a longchain 4,5-dimethylalkanes **4,5-n**.

In the sources we use [2,3], there is PMR spectrum of the sole representatives of 4,5-dimethylalkanes **4,5-n** family – the symmetrical 4,5-dimethyloctane **4,5-h**. In its PMR spectrum the authors [2] led an unique attribution the proton signals. They identified two stereoisomers in spectrum and attribute every signal to each of these isomers protons. Unfortunately, some of the methylene and methine protons (for each of the isomers) signals values are given in the form of a fairly narrow range of values, so the ***BSP*** values of such protons we take equal the arithmetic mean of the interval given by the authors [2]. Thus, for the interval 1.34-1.40 ppm let's take the ***BSP*** value equal the arithmetic mean of 1.37 ppm, and for the interval 1.24 - 1.29 ppm – the ***BSP*** value equal to 1,265 ppm.Then the maximum difference the ***BSP*** value which we are attribute from the real values of ***BSP*** (range of values) does not exceed 30mlrd. As the molecule of 4,5-dimethyloctane **4,5-h** is symmetrical, for it is sufficient to consider only a fragment of the C-1 to C-4.

The first isomer of symmetrical ***4,5-dimethyloctane*** **4,5-h1**. The values of base ***4,5-h1-B-I*** (in **ppm**)and the "standard" differential ***4,5-h1-I*** (in **mlrd.**) parameters of the first isomer of the symmetrical 4,5-dimethylhexane **4,5-h** designated as **4,5-h1**, are the following: ***4,5-h1-B-1*** = 0.885, ***4,5-h1-1*** = +5; ***4,5-h1-B-2A*** = 1.200, ***4,5-h1-2A*** = -70; ***4,5-h1-B-2B*** = 1.37, ***4,5-h1-2B*** = +100; ***4,5-h1-B-2*** = 1.285, ***4,5-h1-2*** = +15; ***4,5-h1-B-3A*** = 1.040, ***4,5-h1-3A*** = -230; ***4,5-h1-B-3B*** = 1.265, ***4,5-h1-3B*** = -5; ***4,5-h1-B-3*** = 1.155, ***4,5-h1-3*** = -115; ***4,5-h1-B-4*** = 1.37, ***4,5-h1-4*** = +100; ***4,5-h1-B-4'*** = 0.810, ***4,5-h1-4'***= -70.

The second isomer of symmetrical ***4,5-dimethyloctane*** **4,5-h2**. The values of base ***4,5-h2-B-I*** (in **ppm**) and the "standard" differential ***4,5-h1-I*** (in **mlrd.**) parameters of second isomer of the symmetrical 4,5-dimethylhexane **4,5-h** designated as **4,5-h1**, are the following: ***4,5-h2-B-1*** = 0.885, ***4,5-h2-1*** = +5; ***4,5-h2-B-2A*** = 1.265, ***4,5-h2-2A*** = -5; ***4,5-h2-B-2B*** = 1.31, ***4,5-h2-2B*** = +40; ***4,5-h2-B-2*** = 1.290, ***4,5-h2-2*** = +20; ***4,5-h2-B-3A*** = 1.110, ***4,5-h2-3A*** = -160; ***4,5-h2-B-3B*** = 1.230, ***4,5-h2-3B*** = -40; ***4,5-h2-B-3*** = 1.170, ***4,5-h2-3*** = -100; ***4,5-h2-B-4*** = 1.420, ***4,5-h2-4*** = +150; ***4,5-h2-B-4'*** = 0.745, ***4,5-h2-4'*** = -135**.**

The "additional" differential parameters (***4,5-h1'-I*** in **ppm**) of ***4,5-dimethyloctane*** **4,5-h**.(**4,5-h1** and **4,5-h2**).As the subtrahend arithmetic means let's apply the above parameters of the "standard» ***DSP 4n-i***. The parameters of the first isomer **4,5-h1** (***4,5-h1'-i***) are: ***4,5-h1'-1*** = [(+5) – (0)] = **+5**; ***4,5-h1-2*** = [(+15) – (+25)] = **-10**; ***4,5-h1-3*** = [(-115) – -115)] = **0**; ***4,5-h1-4*** = [(+100) – (+115)] = **-15**; ***4,5-h1'-4'*** = [(-70) – (-40)] = **-30**. The parameters of the second isomer **4,5-h2** (***4,5-h2'-i***) are: ***4,5-h2'-1*** = [(+5) – (0)] = **+5**; ***4,5-h2-2*** = [(+20) – (+25)] = **-5**; ***4,5-h2-3*** = [(-100) – -115)] = **-15**; ***4,5-h2-4*** = [(+150) – (+115)] = **+35**; ***4,5-h2'-4'*** = [(-135) – (-40)] = **-95**.

The "aggregated" **"standard" "*4,5-h-i*" and the "additional" "*4,5-h'-i*" differential parameters** for both isomers of ***4,5-dimethyloctane*** **4,5-h**(**4,5-h1** and **4,5-h2**). Let us calculate these parameters as half the sum of the relevant parameters of both isomers and round it to the nearest multiple of 5number. (Since the family of 4.5-dimethylalkanes **4,5-n** in our study is only one compound - the symmetrical 4,5-dimethyloctane **4,5-h** - shown below its parameters take as the average parameters of the whole class of 4,5-dimethylalkanes **4,5-n**: "***4,5-n-i***" and "***4,5-n'-i***"). For comparison in parentheses we give the similar average parameter of the whole 3,4-dimethylalkane **3,4-n** family, in **mlrd.**: ***4,5-h-1*= +5 (≈ -15)**; ***4,5-h'-1* = +5 (≈ -5)**; ***4,5-h-2* ≈ +20**; ***4,5-h'-2* ≈ -10**; ***4,5-h-3* ≈ -110 (≈ -40)**; ***4,5-h'-3* ≈ -10 (≈-5)**; ***4,5-h-4* = +125 (+30)**; ***4,5-h'-4* = +10 (-35)**; ***4,5-h-4'* ≈ -105 (≈ -100)**; ***4,5-h'-4'* ≈ -65 (≈ -65).**

Let us compare obtained the average of the whole class of 4,5-dimethylalkanes **4,5-n** parameters "***4,5-n-i***" and "***4,5-n'-i***" in the hexacarbonic fragment $[-C^{i-1}H^{i-1}{}_2\text{-}C^{i}H^{i}(C^{i'}H^{i'}{}_3)–C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}{}_3)–C^{i+2}H^{i+2}{}_2\text{-}]$, where ***i*** =4, with the same parameters in the same hexacarbonic fragment obtained for the family of 2,3dimethylalkanes **2,3-n**, wherein ***i*** =2 and of 3,4-dimethylalkanes **3,4-n**, wherein ***i*** =3. The comparison we carry out of a tetracarbonic fragment $[-C^{i+1}H^{i+1}{}_2\text{-}C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}{}_3)\text{-}C^{i+3}H^{i+3}{}_2]$, i.e., in the same part above hexacarbonic fragment, wherein the effects of terminal fragments vicinity are minimized in both families of compared dimethylalkanes **N,N'-n**. For the case of the symmetrical 4,5-dimethyloctane **4,5-h** the fragment$[-C^5H^5(C^{5'}H^{5'}{}_3)\text{-}C^6H^6\text{-}]$ coincides with the already discussed fragment$[-C^3H^3{}_2\text{-}C^4H^4(C^{4'}H^{4'}{}_3)\text{-}]$. Let's similize the comparable quantities expressed in mlrd.

***2,3-n-3* = -10** versus ***3,4-n-4* = +30** versus ***4,5-n-5* = +125.** ***2,3-n'-3* = -75** versus ***3,4-n'-4* = -35** versus ***4,5-n'-5* = +10.**

***2,3-n-3'* = -95** versus ***3,4-n-4'* = -100** versus ***4,5-n-5'* = -100.** ***2,3-n'-3* = -75** versus ***3,4-n'-4'* = -65** versus ***4,5-n'-5'* = -65.**

***2,3-n-4* = -80** versus ***3,4-n-5* = -40** versus ***4,5-n-3* = -110.** ***2,3-n'-4* = -10** versus ***3,4-n'-5* = -5** versus ***4,5-n'-3* = -5.**

From the above comparison table one can see quite satisfactory agreement in magnitude (the differences do not exceed│40 **mlrd.**│)of the corresponding "standard" and "additional" differential parameters, except for the parameters characterizing the methine protons H-3 in 2,3-dimethylalkanes **2,3-n**, H-4 in 3,4-dimethylhexane **3,4-f** and H-5 in 4,5-dimethylhexane **4,5-h**. To explain this discrepancy we must remember about that it has been repeatedly said before about the "unreliability of assignments" of the protons entering the polyprotonic multiplet signal in the range of 1.0 -1.5 ppm. Therefore, we can conclude that the second methyl group is introduced to an C-5 atom in mono-4-methylalkanes (i.e. in linear alkanes already having a methyl substituent at C-4) will have a **similar effect on the protons absorption of considered tricarbonic fragment** in the resulting 4,5-dimethylalkanes **4,5-n**, what we previously observed in similar in structure the 2,3- and 3,4-dimethylalkanes families.

3.3. 2. The family of 4,4-dimethylalkanes 4,4-n.

In the spectra of 4,4-dimethylalkanes **4,4-n** family of the general formula: $C^{1}H^{1}{}_{3}\text{-}C^{2}H^{2}{}_{2}\text{-}C^{3}H^{3}{}_{2}\text{-}C^{4}(C^{4'}H^{4'}{}_{3})(C^{4''}H^{4''}{}_{3})\text{-}C^{5}H^{5}{}_{2}\text{-}C^{6}H^{6}{}_{2}\text{-}\ldots\text{-}C^{\omega-1}H^{\omega-1}{}_{2}\text{-}C^{\omega}H^{\omega}{}_{3}$ both "tetracarbon fragment" we are interested $\mathbf{[\text{-}C^{i-1}H^{i-1}{}_{2}\text{-}C^{i}H^{i}(C^{i'}H^{i'}{}_{3})\text{–}C^{i+1}H^{i+1}{}_{2}\text{-}]}$ (***i*** = 4) are **completely overlap one another**, forming a tricarbonic fragment [$\mathbf{\text{–}C^{4}(C^{4'}H^{4'}{}_{3})(C^{4''}H^{4''}{}_{3})\text{-}}$] a similar to analogous fragments discussed earlier in 2,2- and 3,3-dimethylalkanes. Therefore, as in these families of dimethylalkanes it may be appropriate to consider in the 4,4-dimethylalkanes **4,4-n** familiy there is a whole moiety - just the **“pentacarbonic” fragment** $\mathbf{[\text{-}C^{3}H^{3}{}_{2}\text{-}C^{4}(C^{4'}H^{4'}{}_{3})(C^{4''}H^{4''}{}_{3})\text{–}C^{5}H^{5}{}_{2}\text{-}]}$, as moiety that forming the spectral changes from the spectrum of the linear alkane; as well as an additional the methylene group $\mathbf{\text{–}C^{7}H^{7}{}_{2}\text{-}}$ in a longchain 4,4-dimethylalkanes **4,4-n**.

In the sources we use [2,3], there are PMR spectra of only 4,4-dimethylalkanes **4,4-n** representatives: the "asymmetrical "truly longchain”4,4-dimethyloctane **4,4-h**.

Unfortunately, the ***BSP*** values of all methylene protons are given as a single value (the center of the multiplet signal?) equal to 1.17 ppm. Most likely, this value is an average, so the ***BSP*** values of methylene protons will not be discussed. The only subjects to the discussion are the methyl protons ***BSP*** values of the terminal and germinal methyl groups.

In asymmetrical longchain molecule of 4,4-dimethyloctane **4,4-h** let’s consider the values of base ***4,4-h-B-I*** (in **ppm**) and the "standard" differential ***4,4-h-I*** (in **mlrd.**) parameters of methyl protons H-1, H-4' = H-4'' and H-8: ***4,4-h-B-1*** = ***4,4-h-B-8*** = 0.880, ***4,4-h-1 = 4,4-h-8= 0***; ***4,4-h-B-4’*** = ***4,4-h-B-4’’*** = 0.819, ***4,4-h-4’ = 4,4-h-4’’= -61***. The "additional" "rounded" differential parameters ***4,4-h’-I*** (in **mlrd.**) are: ***4,4-h’-1 = 0; 4,4-h’-8*** = [(0) – (-5)] = **-5**; ***4,4-h’-4’ = 4,4-h’-4’’*** =[(-61) – (-40)] = **-20.**

Let us compare of the analogous parameters for the family of 4,4-dimethylalkanes **4,4-n** and of 3,3-dimethylalkanes **3,3-n** family. As the comparison is advisable to carry out of such protons signals, wherein the effects of terminal fragments vicinity are minimized, so the parameters of gem-dimethyl group of 2,2-dimethylalkanes **2,2-n** are excluded from the comparison. It seems appropriate to compare the two pairs of signals from the protons of two gem-methyl groups: [$\mathbf{(C^{3'}H^{3'}{}_{3})(C^{3''}H^{3''}{}_{3})}$] in 3,3-dimethylalkane **3,3-n** family and [$\mathbf{(C^{4'}H^{4'}{}_{3})(C^{4''}H^{4''}{}_{3})}$] in 4,4-dimethylalkanes **4,4-n**.

3,3-n-3’ = 3,3-n-3’’ = -80 versus ***4,4-n-4’ = 4,4-n-4’’ = -60*** ***3,3-n’-3’ = 3,3-n’-3’’ = -45*** versus ***4,4-n’-4’ = 4,4-n’-4’’ = -20.***

From the above data one can see fairly good agreement in magnitude (the differences do not exceed│20 **mlrd.**│)of the corresponding "standard" and "additional" differential parameters. Therefore, we can conclude that the second methyl group is introduced to an C-4 atom in mono-4-methylalkanes (i.e. in linear alkanes already having a methyl substituent at C-4) will have a **similar effect on the protons absorption of** two gem-methyl groups **in considered tricarbonic fragment** [$\mathbf{C^{4}(C^{4'}H^{4'}{}_{3})(C^{4''}H^{4''}{}_{3})}$] in the resulting 4,4-dimethylalkanes **4,4-n**, what we previously observed in similar in structure of 3,3-dimethylalkane **3,3-n** families.

The absorption of two terminal methyl group protons of H-1 and H-8 in the unsymmetrical 4,4-dimethyloctane **4,4-h** within the highest error (±20mlrd.) is not different from the value ***etal-CH₃*= 0.880** ppm in linear alkanes (see above).

3. 4. The estimation of the two methyl substituents introduction into the unsubstituted linear alkane molecule influence on spectral parameters of the resulting dimethylalkane.

We propose the following, logically justified (in our opinion) method of estimating the result of the two methyl groups (substituents) simultaneous introduction into the unsubstituted linear alkane molecule (i.e., the result of the conversion from the linear alkane to dimethylalkanes, in the **n →** $\mathbf{N^1,N^2\text{-}n}$ process). For this purpose we must summarize all above founded **mean values** of the "standard" differential spectral parameters $N^1,N^2\text{-}n\text{-}i$ (calculated above for all "true longchain" dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$**)** of each proton in the resulting molecule of dimethylalkane.

For two magnetically nonequivalent protons of the methylene group (or two magnetically nonequivalent methyl groups) one can take its "aggregated" "standard" "$N^1,N^2\text{-}n\text{-}i$" ($N^1,N^2\text{-}n''\text{-}i$) differential parameters instead. For protons of methylene groups whose "standard" parameters were not considered higher we take zero differential parameter values, i.e., $N,N'\text{-}n\text{-}i$ = $N,N'\text{-}n'\text{-}i$ = 0. We emphasize that the arithmetic mean values of the parameters used are estimated, i.e., accuracy of each of them we estimate of ± 10 **mlrd.** Hence the total result of the calculation will be expected to have even less accurate (we assume the existence of error of ± 50 **mlrd.**).

For those families of dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$, in which two dicarbonic fragments $\mathbf{[(-C^{i}H^{i}(C^{i'}H^{i'}_{3})-]}$ (where **R** = *i*) are **separated by at least three methylene groups** in carbon chain **(i.e.** $\mathbf{N^2 \geq N^1 + 3}$ **)** the above-considered tetracarbonic (and octahydrogenic) fragments $\mathbf{[-C^{i-1}H^{i-1}_{2}\text{-}C^{i}H^{i}(C^{i'}H^{i'}_{3})\text{–}C^{i+1}H^{i+1}_{2}\text{-}]}$ **do not interact with each other**. In such families of dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$ **the "aggregated" (integral) spectral changes** that occurred during the conversion from linear alkanes **n** (not containing methyl substituents) to dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$ are **equal to the sum of the changes** caused by **each separated above tetracarbonic fragment**. These changes are discussed and classified earlier in [1], and so will not be considered here.

Let's consider three types of polycarbonic moieties which are formed by overlapping of two above tetracarbonic fragments, **(i.e.** $\mathbf{N^2 < N^1 + 3}$**)**. This fragments are: heptacarbonic (and 14H) fragment $[-C^{i-1}H^{i-1}_{2}\text{-}C^{i}H^{i}(C^{i'}H^{i'}_{3})\text{-}C^{i+1}H^{i+1}_{2}\text{-}C^{i+2}H^{i+2}(C^{i+2'}H^{i+2'}_{3})\text{-}C^{i+3}H^{i+3}_{2}\text{-}]$ ($\mathbf{N^2 = N^1 + 2}$), hexacarbonic (and 12H) fragment $[-C^{i-1}H^{i-1}_{2}\text{-}C^{i}H^{i}(C^{i'}H^{i'}_{3})\text{-}C^{i+1}H^{i+1}(C^{i+1'}H^{i+1'}_{3})\text{-}C^{i+2}H^{i+2}_{2}\text{-}]$ ($\mathbf{N^2 = N^1 + 1}$) and pentacarbonic (and 10H) fragment $[C^{i-1}H^{i-1}_{3}\text{-}C^{i}(C^{i'}H^{i'}_{3})(C^{i''}H^{i''}_{3})\text{–}C^{i+1}H^{i+1}_{2}\text{-}]$ ($\mathbf{N^2 = N^1}$). Each of 3 these fragments, as described above, we consider as a whole. For each type of dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$ let's consider two variants of the "aggregated" spectral changes: a) for shortchain families (when $\mathbf{N^1 = 2}$) and b) for "more longchain" families (when $\mathbf{N^1 > 2}$). This division into two variants due to the presence of "**the effects of the end of the chain**" in the families of 2,N-dimethylalkanes $\mathbf{2,N^2\text{-}n}$. Obviously, the more correct settings are "more longchain" families $\mathbf{N^1,N^2\text{-}n}$ (when $\mathbf{N^1 > 2}$), free from the abovementioned "end effect".

Let's estimate **the "aggregated" (integral) spectral changes denoted as** Σ $N^1,N^2\text{-}n\text{-}i$ that occurred during the conversion from linear alkanes **n** to the families of **2,4-n** and **3,5-n** dimethylalkanes, which containing the above heptacarbonic moiety. All required **mean values** of the "standard" differential spectral parameters $N^1,N^2\text{-}n\text{-}i$ are given in parts 3. 1. 3 and 3. 2. 3.

Variant A (***2,4-n-1* = -40**; ***2,4-n-2*** **= +360**; ***2,4-n-3*** **= -240**; ***2,4-n-4*** **= +150**; ***2,4-n-5* = -95**, and: ***2,4-n-2'*** **= -15**, ***2,4-n-4'*** **= -55**. So the "aggregated" spectral changes Σ $N^1,N^2\text{-}n\text{-}i$ for 15 protons are: [3 x (-40)] + [1 x (+360)] +[2 x (-240)] + [1 x (+150)] + [2 x (-95)] + [3 x (-15)] + [3 x (-55)] = (-120+360-480+150-190-45-165) = **-490.**

Variant B (***3,5-n-2* = -60**; ***3,5-n-3*** **= +130**; ***3,5-n-4* = -220**; ***3,5-n-5*** **= +130**; ***3,5-n-6* = -60**, and: ***3,5-n-3'*** **= -55**, ***3,5-n-5'*** **= -55**. So the "aggregated" spectral changes Σ $N^1,N^2\text{-}n\text{-}i$ for 14 protons are: [2 x (-60)] + [1 x (+130)] +[2 x (-220)] + [1 x (+130)] + [2 x (-60)] + [3 x (-15)] + [3 x (-55)] = (-120+130-440+130-120-165-165) = **-750.**

Let's estimate **the "aggregated" (integral) spectral changes** that occurred during the conversion from linear alkanes **n** to the shortchain families of **2,3-n** and let's assume the mean "standard" differential spectral parameters of two "more longchain" families: **3,4-n and 4,5-n** dimethylalkanes (named as $N^1,N^2\text{-}n\text{-}i$), which containing the above hexacarbonic moiety as given in parts 3. 1. 4, 3. 2. 4 and 3. 3. 1.

Variant A (***2,3-n-1* = -85**; ***2,3-n* -2** = **+280**; ***2,3-n* -3 = -10**; ***2,3-n* -4** = **-80**; and: ***2,3-n* -2′ = -45**, ***2,3-n-3′* = -95**. So the “aggregated” spectral changes **Σ *N^1,N^2-n-i*** for 13 protons are: [3 x (-85)] + [1 x (+280)] +[1 x (-10)] + [2 x (-80)] + [3 x (-45)] + [3 x (-95)] = (-255+280-10-160-135-285) = **-565.**

Variant B (parameters ***4,5-n-i*** are given with parentheses; and parameters ***3,4-n-i*** are given without parentheses): (***N^1,N^2-n-(i-1)* = -40 (-110)**; ***N^1,N^2-n-(i)*** = **+30 (+125)**; ***N^1,N^2-n-(i+1)*** = **+30 (+125)**; ***N^1,N^2-n-(i+2)*** = **-40 (-110)**; and ***N^1,N^2-2′* = -100 (-105)**; ***N^1,N^2-3′* = -100 (-105)**. So the “aggregated” spectral changes **Σ *N^1,N^2-n-i*** for 12 protons are: **[-700** + **(-820)]/ 2** = **-760.**

Let's estimate **the “aggregated” spectral changes** that occurred during the conversion from linear alkanes **n** to the shortchain families of **2,2-n** and mean parameters of "more longchain" families: **3,3-n** dimethylalkanes, which containing the above pentacarbonic moiety. All required **mean values** of the “standard” differential spectral parameters ***N^1,N^2-n-i*** are given in parts 3. 1. 5, 3. 2. 5 and 3. 3. 2.

Variant A: (***2,2-n-1* = -20**; ***2,2-n-3* = -100**; and: ***2,2-n-2′* = -20**, ***2,2-n-2″* = -20**. So the “aggregated” spectral changes **Σ *N^1,N^2-n-i*** for 11 protons are: [9 x (-20)] + +[2 x (-100)] = (-180-200) = **-380.**

Variant B: (***3,3-n-2* = -65**; ***3,3-n-4* = -120**; and: ***3,3-n-3′* = -75**, ***3,3-n-3″* = -75**. So the “aggregated” spectral changes **Σ *N^1,N^2-n-i*** for 10 protons are: **-820.**

These estimations show **that all three types of integral changes are negative** but notably differ in magnitude. The every of shortchain families of dimethylalkanes **2,N^2-n** (when **N^1 = 2**) has the integral change **Σ *N^1, N^2-n-i* (-490, -565, -380**) much less than the other three types of longchain families of dimethylalkanes **N^1,N^2-n** (**-750, -760, -820**) which are substantially equal. Let’s note that the above values (**-780 ± 40 mlrd.**) of "integral spectral changes" **Σ *N^1,N^2-n-i*** that occur when into alkane molecule **n** are introduced two methyl groups (i.e., in the **n →** **N^1,N^2-n** process), ***exceed twice*** the discussed previously [1] analogous "integral spectral changes" **Σ *N^1,N^2-n-i*** (**-350 ± 30 mlrd.**) that occur when introducing only one methyl group into the molecule of an alkane **n** (i.e. in the **n → Nn** process).

Note also that the value of "integral spectral changes» **Σ *N^1,N^2-n-i*** (**-470 ± 100 mlrd.**) for shortchain families of dimethylalkanes **2,N^2-n** (when **N^1 = 2**) is **much less** the similar values for the other three types of longchain families of dimethylalkanes **N^1,N^2-n** (**-780 ± 40 mlrd.**). A similar situation has been described previously for the case monomethylalkanes when integrated upfield shift in the family of shortchain 2-methylalkanes **2n** was significantly less than that for the longchain N-methylalkanes **Nn** (**N** = 3,4,5).

Given the approximate nature of these calculations, we can conclude that the **introduction of two methyl substituent in the linear alkane molecule n, leading to the formation of dimethylalkants N^1,N^2-n, accompanied by a significant upfield shift of “aggregated” signas Σ *N^1,N^2-n-i* of remaining and newly formed types of protons**.

The estimation of the spectral changes that occur when the second methyl group (substituent) introduction into the monomethyl substituted linear alkane molecule **Nn** resulting the conversion it to dimethylalkanes **N^1,N^2-n** (i.e., **Nn** → **N^1,N^2-n** process) we consider inappropriate. Each family of dimethylalkanes **N^1,N^2-n** can be obtain from monoalkanes **Nn** (as precursor) by one of two possible ways: either by introducing the second methyl group into **N^2** position of monoalkane **N^1n** (**N^1n** → **N^1,N^2-n** process), or by introducing the second methyl group into **N^1** position of monoalkane **N^2n** (**N^2n** → **N^1,N^2-n** process). **Such ways uncertainty** of obtaining the dimethylalkanes **N^1,N^2-n** from monomethylalkane **Nn** **not establish that a single set** of ***integral spectral changes*** occurring during the above conversion **Nn** → **N^1,N^2-n.**

Furthermore **the comparison** of the dimethylalkanes **N^1,N^2-n** (when **N^1+2 ≥ N^2**) ***BSP*** values with of two tetracarbonic (and octahydrogenic) fragments **$[-C^{i-1}H^{i-1}{}_2-C^iH^i(C^{i'}H^{i'}{}_3)–C^{i+1}H^{i+1}{}_2-]$** the ***BSP*** values in two molecules of monoalkane **N^1n** and **N^2n** **is uncorrect** because of the different number of compared protons. So all three polycarbonic (heptacarbonic, hexacarbonic and pentacarbonic) fragments in dimethylalkanes **N^1,N^2-n** contain **10 (11), 12 (13) or 14 (15) hydrogen atoms**, respectively, whereas two tetracarbonic (and octahydrogenic) fragments in two monoalkane **N^1n** and **N^2n** contain **16 (17) hydrogen atoms.**

4. General conclusions

1. We have analyzed the protons chemical shifts values in the PMR spectra of dimethylalkanes compounds of general formula **N^1,N^2-n** (when **n** is the letter designation of linear alkane, and **N^1, N^2** are the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**). It is calculated the individual (***N^1,N^2-n-i***) and arithmetic means (***N^1,N^2-n-i***) “standard” differential parameters (the difference between absorption of studied proton in **N^1,N^2-n** and its absorption in the **n**). It is calculated the differences between the total values of ***N^1,N^2-n-i*** parameters for **all protons in the molecule** of **N^1,N^2-n**. These values are called the "integral spectral changes” that occur in process **n →** **N^1,N^2-n**, and designated as **Σ** ***N^1,N^2-n-i***.

2. It is shown that for those types of the dimethylalkanes **N^1,N^2-n** families, in which the carbon atoms **N^1** and **N^2** are separated by three or more methylene groups (i.e. **$N^2 \geq N^1 + 3$**) , the total parameter **Σ** ***N^1,N^2-n-i*** is the **arithmetic sum of the two values** of the "integral spectral changes” **Σ** ***N-n-I***, which are calculated for monomethylalkanes **Nn**. These sum parameters are described previously [1] and are equal: **Σ** ***N^1-n-i*** for monomethylalkane **N^1n** and **Σ** ***N^2-n-i*** for monomethyalkanes **N^2n**.

3. In the three types of the dimethylalkanes **N^1,N^2-n** families, in which the carbon atoms **N^1** and **N^2** are separated by less than two methylene group (i.e., **$N^1+2 \geq N^2$**), the value of **Σ** ***N^1,N^2-n-i*** parameter is **determined by the absorption of polycarbonic (heptacarbonic, hexacarbonic and pentacarbonic) fragments** in the molecule of the dimethylalkanes **N^1,N^2-n**, which we **regard as a whole**. These fragments include protons linked to two carbon atoms **N^1** and **N^2** with attached there to two methyl groups and the protons of methylene groups located in the alkyl chain before (**N^1-1**) and after (**N^2+1**) and a methylene group (if present) that is located between the atoms **N^1** and **N^2**.

4. All three types of the sum parameter **Σ** ***N^1,N^2-n-i*** that occur when into alkane molecule **n** are introduced two methyl groups (i.e., in the **n →** **N^1,N^2-n** process when **$N^1+2 \geq N^2$**) **are negative (upfield)** but notably differ in magnitude. (***Σ N^1,N^2-n-i < 0***)

5. The values of the sum parameter (**Σ** ***N^1,N^2-n-I*** = **-470 ± 100 mlrd.**) of the shortchain families of dimethylalkanes **2,N^2-n** (when **N^1 = 2**) is **much less** three types of the longchain families of dimethylalkanes **N^1,N^2-n** (when **N^1** = 3,4) (**Σ** ***N^1,N^2-n-i*** = **-780 ± 40 mlrd.**). A similar situation has been described previously for the case monomethylalkanes when integrated upfield shift in the family of the shortchain 2-methylalkanes **2n** (**Σ** ***2-n-i***) was significantly less than the sum parameter (**Σ** ***N-n-i***) for the longchain N-methylalkanes **Nn** (when **N** = 3,4,5).

6. The values of "integral spectral changes" **Σ** ***N^1,N^2-n-i*** = **-780 ± 40 mlrd.** that occur in process **n →** **N^1,N^2-n** (when **N^1** = 3,4), ***exceed twice*** the discussed previously [1] analogous "integral spectral changes" (***Σ N-n-i*** = **-350 ± 30 mlrd.**).

References

[1] V. Mizyuk and V. Shibanov. Accompanied paper to ECSOC-17.