The influence of the all three methyl group positions in trimethylalkane molecules on the chemical shifts values of all protons in the ^{1}H NMR spectra

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Abstract. The protons chemical shifts values in the PMR spectra of trimethylalkanes of general formula $\mathbf{N^1,N^2,N^3\text{-}n}$ (when **n** is the letter designation of linear alkane, and $\mathbf{N^1}$, $\mathbf{N^2,N^3}$ are the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**) of 4 trimethylalkane families (**2,2,5-n; 2,2,4-n; 2,2,3-n** and **2,3,4-n**) have analyzed. It is calculated and discussed the individual ($\boldsymbol{N^1,N^2,N^3\text{-}n\text{-}i}$), the arithmetic means ($\boldsymbol{\underline{N^1,N^2,N^3\text{-}n}\text{-}i}$) "standard" differential parameters (the difference between absorption of studied proton in $\mathbf{N^1,N^2,N^3\text{-}n}$ and its absorption in the **n**) and the "integral spectral changes" $\boldsymbol{\Sigma\ \underline{N^1,N^2,N^3\text{-}n}\text{-}i}$ that occur in process $\mathbf{n} \rightarrow \mathbf{N^1,N^2,N^3\text{-}n}$). Also it is calculated and discussed the individual first ($\boldsymbol{N^1,N^2,N^3\text{-}n'\text{-}i}$), second ($\boldsymbol{N^1,N^2,N^3\text{-}n''\text{-}i}$) and the arithmetic means ($\boldsymbol{\underline{N^1,N^2,N^3\text{-}n'}\text{-}i}$) additional differential parameters (the difference between absorption of studied proton in $\mathbf{N^1,N^2,N^3\text{-}n}$ and its absorption in the correspondent monomethylalkane **Nn** or dimethylalkanes $\mathbf{N^1,N^2\text{-}n}$**).**

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

1. Introduction

1.1. General comments

In a previous reports [1, 2], we describe the results of the study of chemical shift values of all protons in the mono- and dimethylalkanes molecules. The next step planned to study the effect of the introduction of a third methyl group in the alkyl chain of the dimethylalkanes on NMR spectral parameters of resulted trimethylalkanes molecules. It was shown that the introduction of the second methyl group into monomethylalkane molecule at such positions of the alkyl chain which leads to dimethylalkanes molecule with two methyl groups separated by three or more methylene groups results the formation of a new the so-called "tetracarbonic fragment$[\text{-}C^{N-1}H^{N-1}{}_2\text{-}C^{N}H^{N}(C^{N'}H^{N'}{}_3)\text{–}C^{N+1}H^{N+1}{}_2\text{-}]$. When in the newly formed dimethylalkane molecule with two methyl groups separated by less than two methylene groups we observe the polycarbonic (heptacarbonic, hexacarbonic and pentacarbonic) fragments, which we regard as a whole. It is interesting to **examine the change in the PMR spectra of trimethylalkanes** formed by introduction of the third methyl group into dimethylalkane molecule **as the result of the interaction between aforesaid fragments** when they differed the types and their relative position in the molecule.

1.2. Objects of research

1. 2. 1. Long-, mid- and shortchain alkanes.

Linear alkanes as well as studied trimethylsubstituted their derivatives (trimethylalkanes) depending upon the carbon chain length we conditionally divide into several groups [1, 2]. First of all, it is longchain molecules (the chain of which comprises more than 10 carbon atoms), then, midchain (which chain comprises from 5 to 10 carbon atoms) and, at last, shortchain (the chain of which comprises from 2 to 4 carbon atoms) groups.

1. 2. 2. Peculiarities of trimethylalkanes structure denotation.

As previously [1,2] we designate each molecule of trimethylalkane «**N^1,N^2,N^3-n**» consists of two parts: the first two numeric of the **N^1** ,**N^2** and **N^3** (**N^3** ≥ **N^2** ≥ **N^1**) separated by commas indicates the position of three methyl groups in the alkyl chain (i.e., **N^1, N^2,N^3** are the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**). Besides, **N^1,N^2,N^3** letters specified family of trimethylalkanes). Then, with a hyphen small letter indicate the name of the alkane. Numbering started with the shortest chain of methane ("a"), although among considered trimethylalkanes there are no derivative of methane "a", ethane «b», and propane «c». The symbol "d" denotes butane, «e»- pentane, «f»- hexane, «g» - heptane and «h»-octane. The different isomers of trimethylalkanes are formed depending on the occurrence place of all three methyl groups in the chain («**N^1**», «**N^2**» and «**N^3**»). "Near end" methyl group is marked by the number **N^1**, and "far end" – by the number **N^3**. For example, 2,3,4-trimethylpentane denoted as «**2,3,4-e**».This example shows the numbering of carbon and hydrogen atoms in all of the families of «**N^1,N^2,N^3-n**» trimethylalkanes.

For instance, the compounds of «**2,3,4-n**» and «**2,2,5-n**» families have the structure:

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

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

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 [1]. 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 -C^N- 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], in dimethylalkane molecule there are new the so called "gem-dimethylalkane fragment" when **N^1** = **N^2** (or **N^2** = **N^3**) with a quaternary carbon atom [2]. All indicated fragments are present in trimethylalkane molecules «**N^1,N^2,N^3-n».**

As previously [2] we use the notions of "one-carbonic fragments", "dicarbonic fragment" (for instance, "methine fragment" [-$C^NH^N(C^{N'}H^{N'}{}_3)$-]) and "three-carbonic gem-dimethyl moiety" - fragment [-$C^N(C^{N'}H^{N'}{}_3)(C^{N''}H^{N''}{}_3)$-] in viewed trimethylalkane molecules «**N^1,N^2,N^3-n».**

In alkyl chain of each type of trimethylalkane families **N^1,N^2,N^3-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 2,2,5-trimethylhexane «**2,2,5-f-5'**», are designated as H-5' . Accordingly, the proton chemical shift of this methyl group is indicated (see below) as «$\boldsymbol{\delta}^{\mathbf{H,2,2,5\text{-}f}}{}_{5'}$». In gem-trimethylalkanes (for example, 2,2,5-trimethylhexane **2,2,5-f**) both "mid" methyl groups denoted as «-$C^{2'}H^{2'}{}_3$» and «-$C^{2''}H^{2''}{}_3$», and their carbon and hydrogen atoms as: C-2', C-2", H-2' and H-2''.

In the information sources we use [3, 4] lack the spectral data for such longchain trimethylalkanes that contain the first "near end" methyl group only at C-3 (**N^1** = 3) or longer in the chain. Therefore, our analysis is limited to a five substances of four families up to **2,N^2,N^3**-trimethylalkanes (**2,N^2,N^3-n**).

Signal of proton in molecule of trimethylalkane «**N^1,N^2,N^3-n**» in general designated as «$\boldsymbol{\delta}^{\mathbf{H,N1,N2,N3\text{-}n}}{}_{i}$». 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^3-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 $\boldsymbol{\delta}^{\mathbf{H,N1,N2,N3\text{-}n}}{}_{iA}$ and downfield ("lowfield") – by the letter "B" ($\boldsymbol{\delta}^{\mathbf{H,N1,N2,N3\text{-}n}}{}_{iB}$). For example, "far end" α- methylene protons H-5A and H-5B in 2,2,4-trimethylhexane **2,2,5-f** denoted as $\boldsymbol{\delta}^{\mathbf{H,2,2,4\text{-}f}}{}_{5A}$ ("upfield" proton), and "lowfield" as $\boldsymbol{\delta}^{\mathbf{H,2,2,4\text{-}f}}{}_{5B}$. The absorption or ***magnetically equivalent*** protons (for example, $\delta^{H,2,2,4f}{}_{3}$), or ***"total" absorption two magnetically nonequivalent protons*** (for example, $\delta^{H,2,2,4f}{}_{5}$, see below) is denoted without the use of the signs " A" and "B".

Initially we discuss three families of trimethyl-substituted gem-trimethylalkanes **2,2,N^3-n**, and then the only compound of last family "**2,3,4-n**" - 2,3,4-trimethylpentane (**2,3,4-e**). First of all we shall consider such gem-trimethylalkanes, in which the third methyl group is as far away from the first methyl group (the number **N^3** is the maximal, ie, **N^3** = ω). So firstly we shall consider the family of the gem-dimethylalkanes when **N^1** = **N^2 and N^3** = ω (in our case - 2,2,5-trimethylhexane «**2,2,5-f**»). Then consequently the family of 2,2,4-trimethylalkanes (**2,2,4-e** and **2,2,4-f**) and 2,2,3-trimethylalkanes (**2,2,3-d**). And finally, the abovementioned family of «**2,3,4-n**» –ie, 2,3,4-trimethylpentane (**2,3,4-e**).

The discussion of spectral parameters for each of the ***i***-type protons in all of the trimethylalkane ««**N^1,N^2,N^3-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 three "mid" methyl groups (if they exist in the molecule) – first one that is closer to the beginning of the chain, then the one, and finally 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 (if they exist in the molecule).

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 grounded on the observation of their reliability and compatibility. We used only chemical shift values obtained in deuteriochloroform $CDCl_3$ as a solvent and presented in the reference book [3, 4]. Spectra obtained in other solvent, e.g. CCl_4, we do not examine here. The chemical shift parameters given in [3] (which are usually given up to 0.001 ppm) were obtained using instruments with different frequency: low-frequency (90 MHz) and high-frequency (300 or 400 MHz). "Low-frequency" parameters used only in the absence of "high-frequency" values. The authors of data represented in [3] give their own attribution of spectra signals to the absorption of definite types of hydrogen atom nuclei. The authors of data represented in [4] (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 trimethylalkane **N^1,N^{2}N^3-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 signals are triplet signals of methyl end groups; the signals of middle methyl groups (doublets) and the singlet signals of nine protons in the compounds **2,2,N^3-n** families. 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 trimethylalkanes of **2,N^2,N^3-n** families, denoted above as "$\delta^{H,2,N2,N3\text{-}n}{}_{i}$", are shown at the beginning of corresponding sections. These values we called the **basic spectral parameters** (shortly, ***BSP***) of protons absorption. If the ***BSP*** value ($\delta^{H,N1,N2,N3\text{-}n}{}_{i}$) is used in both sources [3 and 4] , both figures are given.

The calculated values of **differential spectral parameters** (shortly «***DSP***»), referred to as $\Delta\delta^{H,2,N2,N3\text{-}n}{}_{i}$, 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^2,N^3-n** taken from [3 and 4], are rounded to the nearest number divisible by 0.005 ppm. We estimate the inaccuracy of measurements as ± 0.02 ppm (20 **mlrd.**, see below).

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

3. Discussion of results

Base spectral parameters. As mentioned above, the chemical shift of the studied proton (i.e., its ***BSP***) in the common designation system referred to as "$\delta^{H,2,N2,N3-n}{}_{i}$" 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 we repeatedly use a new system [2] of designation for each parameter $\delta^{H,2,N2,N3-n}{}_{i}$. In each case the newly introduced designation is duplicated the old one (i.e., with using of common superscript and subscript symbols such as "$\delta^{H,2,N2,N3-n}{}_{i}$"). The ***BSP*** values ("$\delta^{H,2,N2,N3-n}{}_{i}$") in the text are marked with italic black bold font as "***2,N^2,N^3-n-B-i***". The symbol "***B***" indicates that this parameter is basic (***BSP***), and it introduced in order to distinguish the basic parameter from similar abbreviations for the differential spectral parameters (abbreviated ***DSP***, see below). In the above example of the 2,2,5-trimethylhexane **2,2,5-f** the symbol «***2,2,5-h-B-5’***» ($\delta^{H,2,2,5-h}{}_{5'}$) 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 trimethylalkanes **2,N^2,N^3-n** we calculated the arithmetic mean value [1] of the discussed parameter referred to as the ***underlined*** symbol «***2,N^2,N^3-n-B-i***».

Differential spectral parameters. As previously [2], the difference between the chemical shift of the every ***i***-th proton in discussed trimethylalkane **2,N^2,N^3-n** and the same ***i***-th type of protons in the "standard (etalon) compound”, which we denote as (***etal***), we designate as the **differential spectral parameter** «$\Delta\delta^{H,2,N2,N3-n}{}_{i}$» (abbreviated ***DSP***). Depending on tasks it may be selected the ***different etalon compounds***. The ***DSP*** parameters of all of the discussed trimethylalkanes **2,N^2,N^3-n** are calculated for each of the ***i***- type proton as follows: $\Delta\delta^{H,2,N2,N3-n}{}_{i} = \delta^{H,2,N2,N3-n}{}_{i} - \delta^{H,etal}{}_{i}$, and in our proposed system of notation as : ***D-2,N^2,N^3-n-i*** = ***2,N^2,N^3-n-B-i*** - ***etal-B-i***. The differential parameters differ from the base ones so that **they have the sign** " + " or " - ". If the signal ***2,N^2,N^3-n-B-i*** ($\delta^{H,2,N2,N3-n}{}_{i}$) is located in a stronger field than the standard signal (***etal-B-i***), then the differential parameter ***D-2,N^2,N^3-n-i*** has the sign " minus" , and vice versa.

As previously, the **“standard”** differential spectral parameters we denote a shorter red bold italic symbol: (***DSP*** = ***2,N^2,N^3-n-I*** instead of «***2,N^2,N^3-n-D-i***»), wherein no letter «D». The **"standard"** differential parameters of **methyl group protons** is calculated as follows ***2,N^2,N^3-n-i*** = ***2,N^2,N^3-n-B-i*** – **0.880 ppm** (or: $\Delta\delta^{H,2,N2,N3-n}{}_{i} = \delta^{H,2,N2,N3-n}{}_{i}$ – **0.880** ppm). Similarly, the **"standard"** differential parameters of **methylene and methine protons** is calculated as follows : ***2,N^2,N^3-n-i*** = ***2,N^2,N^3-n-B-i*** – **1.270** ppm (or $\Delta\delta^{H,2,N2,N3-n}{}_{i} = \delta^{H,2,N2,N3-n}{}_{i}$ – **1.270 ppm**) and has the same signs. The values of "standard" differential parameters ***DSP*** = ***2,N^2,N^3-n-I*** expressed in billionths parts (**mlrd.**), i.e. $\Delta\delta^{H}$ x 1000.

In addition to **"standard” *DSP*** sometimes may be used other **"additional"** type of ***DSP***, with blue color and with a stroke, that is, ***DSP’ = 2,N^2,N^3-n’-i***. As the "etalon" compound to calculate this type of ***DSP*** we usually use the “family” of corresponding monomethyl or dimethyl alkanes. As the value of "etalon parameter" is usually taken is the arithmetic mean of ***BSP***, which in [1,2] is designated as ***N-B-i***. Hence: ***DSP’*** = ***2,N^2,N^3-n’-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-CH$_3$*** **= 0.880 ppm ± 0.020 ppm** (i.e., in the range from 0.860 ppm to 0.900 ppm) and values of methylene and methine groups ***BSP*** fall into the "strip" values ***etal-CH$_2$*** **= 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". 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".

We hope, that used here methods of comparisons of corresponding parameters (base and differential) allows us to find the regularities of protons BSP values taking place with the introduction of the first, second and third methyl groups into molecules of linear alkanes.

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

To calculate the family of **2,2,N^3-n** trimethylalkanes "**additional**" values of ***DSP'***, let us first of all bring to mind that the "pentacarbonic fragment", including carbon atoms C^1, C^2, $C^{2'}$, $C^{2''}$ and C^3, is present in every type of **2,2,N^3-n** trimethylalkanes. It seems likely that the arithmetic mean parameters of similar "pentacarbonic fragments", which were calculated for a family of 2,2-dimethylalkanes **2,2n** [2], will be suitable for considered **2,2,N^3-n** trimethylalkanes families. Such calculated mean parameters of the "standard" ***DSP*** (*2,2-n-i*, expressed in **mlrd.**) are equal to: *2,2-n-1* = **-20mlrd.**; *2,2-n-3*= **-100mlrd**. The further the third methyl group (**N^3**) will be located along the chain in **2,2,N^3-n** trimethylalkanes, the more, in our opinion, will be the probability of coincidence of these figures with the experimental data.

Let's note that in all compounds of **2,2,N^3** families the main carbon chain of the alkane is not long (ie, these compounds can not be regarded as longchain, rather they are "midchain" or "even shortchain"). On the contrary, a compound such as 2,2,3- trimethylbutane **2,2,3-d** we do not think **linear** alkane derivatives at all. It is, in our opinion, a typical representative of the " branched " alkane . With some reservations, as the "linear" can only be considered hexane derivatives : 2,2,4- (**2,2,4-f**) and 2,2,5-trimethylhexanes (**2,2,5-f**), whereas 2,2,4-trimethylpentane is (**2,2,4-e**) rather is a "branched" than "linear" alkane. These observations are important in terms of the interpretation of the spectral data given for ***BSP*** values of trimethylalkanes **2,2,N^3** in two used sources [2, 3].

3. 1. 1. The Family of 2,2,5-trimethylalkanes (2,2,5-n).

In the family of 2,2,5-trimethylalkanes **2,2,5-n** of the general formula: $C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)–C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5(C^{5'}H^{5'}_3)–C^6H^6_2\text{-}\ldots\text{-}C^{n-1}H^{n-1}_2\text{-}C^nH^n_3$ the carbon atoms in which there are branching (C-2 and C-5), are separated by two methylene groups ($\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}$). Therefore, except the abovementioned "pentacarbonic fragment" $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)–C^3H^3_2\text{-}]$, the most interesting to us is tetracarbonic fragments $[\text{-}C^4H^4_2\text{-}C^5H^5(C^{5'}H^{5'}_3)–C^6H^6_2\text{-}]$. These both fragments do **not overlap one another**, but **"touching each other"**. So for a family of 2,2,5-trimethylalkanes **2,2,5-n** we can expect the almost complete lack of influence of the third methyl group **N^3** (at C-5) on the ***BSP*** values of the pentacarbonic molecule fragment **C-1 - C-3.** We can expect the similar lack of influence of the molecule fragment **C-1 - C-3** at the abovementioned second tetracarbonic fragment of the molecule (**C-4 - C-6).**

In the sources we use [2,3] there is PMR spectra of only representative - 2,2,5-trimethylhexane **2,2,5-f**. We emphasize, that the spectrum of it was obtained at a low frequency instrument (90 MHz), ie with less accuracy. Unfortunately, the ***BSP*** values of all four methylene protons (two protons H-3 and the two protons H-4) are equal to 1.14 ppm (ie parameters ***2,2,5-f-B-3*** = ***2,2,5-f-B-4*** = 1.14 ppm). This fact is already suspicious, considering that the specnrum is a "low-frequency", although we can't exclude such a case, when these values are identical. Considering that the low-frequency instrument was used, it's more likely, this abovementioned value is an average one. On the other hand the average value of mean parameter ***2,2-n-B-3*** = ≈ 1.15 ÷ 1.20 ppm in the spectra of 2,2-dimethylalkanes **2,2-n** families is controversial (or rather, not sufficiently substantiated). So the ***DSP*** values of methylene protons $–C^3\underline{H}^3_2\text{-}$ and $\text{-}C^4\underline{H}^4_2\text{-}$ (parameters *2,2,5-f-3* and *2,2,5-f-4*) will not be discussed. The only subjects to the discussion are the methyl protons ***BSP*** values of the germinal (H^1, $H^{2'}$and $H^{2''}$) and terminal ($H^{5'}$ and H^6) methyl groups, as well as methyne proton (H^5) ***BSP*** values of the methyne group.

In molecule of 2,2,5-trimethylhexane **2,2,5-f** let's consider that the values of base ***2,2,5-f-B-i*** (in **ppm**) and the "standard" arithmetic mean value of the differential parameters *2,2,5-f-i* (in **mlrd.**) of methyl protons H-1, H-2', H-2", H-5' and H-6 are equal: ***2,2,5-f-B-1*** = ***2,2,5-f- B-2'*** = ***2,2,5-f- B-2''*** = 0.862, ***2,2,5-f-1* = *2,2,5-f-2'* = *2,2,5-f-2''* = -18**; ***2,2,5-f-B-5'*** = ***2,2,5-f-B-6*** = 0.88; ***2,2,5-f-5'* = *2,2,5-f-6* = 0**. Methine parameters are equal to: ***2,2,5-f-B-5*** = 1.44; ***2,2,5-f-5* = +170**.

As said before [2] in the spectra of 2,2-dimethylalkanes **2,2-n** families we considered the **"pentacarbonic" fragment** $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)–C^3H^3_2\text{-}]$, as the **moiety that forming the spectral changes** from the spectrum of the linear alkane. This fragment contains in [2] the following mean spectral data: ***2,2-n-1*= -20mlrd., *2,2-n-3*= -100mlrd.**

3.1.1.1. Calculations of "additional" differential parameters *2,2,5-f'-1* and *2,2,5-f'-5'.*

So the "additional" differential parameters *2,2,5-f'-1* (*2,2,5-f'-1 = 2,2,5-f'-2' = 2,2,5-f'-2''*) we calculated as the difference between the "standard" differential parameter ***2,2,5-f-1*** in 2,2,5-trimethylhexane **2,2,5-f** and "standard" mean differential parameters ***2,2-n-1*** in abovementioned 2,2-dimethyalkanes **2,2-n.** Hence the calculated "additional" "rounded" differential parameter *2,2,5-f'-1* (in **mlrd.**) is equal to: *2,2,5-f'-1 = 2,2,5-f'-2' = 2,2,5-f'-2''=* [(-18) – (-20] ≈ **0 mlrd.**

As stated above, the protons H-3 parameters (as well as the protons H-4 parameters, see below) not discussed here.

The tetracarbonic fragment $[-C^4H^4{}_2-C^5H^5(C^{5'}H^{5'}{}_3)–C^6H^6{}_2-]$ (in case of 2,2,5-trimethylhexane **2,2,5-f** this fragment is equal to $-C^4H^4{}_2-C^5H^5(C^{5'}H^{5'}{}_3)–C^6H^6{}_3$) can be regarded as a tetracarbonic fragment $[C^1H^1{}_3-C^2H(C^{2'}H^{2'}{}_3)–C^3H^3{}_2-]$ in family of mono-2-methylalkanes **2n**, for which in [1] the following mean spectral parameters are listed: ***2n-1* = -15**; ***2n-2*** = **+250**; ***2n-3* = -110**; ***2n-4*** = **-10**; ***2n-ω* = + 5** and ***2n-2'*= -15**.

Similarly we can calculate the "additional" differential parameter *2,2,5-f'-6* (*2,2,5-f'-5'= 2,2,5-f'-6*) as the difference between the "standard" differential parameter ***2,2,5-f-6*** in 2,2,5-trimethylhexane **2,2,5-f** and rounded "standard" mean differential parameters ***2n-1*** in abovementioned 2-methyalkanes **2-n:** *2,2,5-f'-6* = [0 - (-15)] = **+15 mlrd**. Similarly the "additional" differential parameter *2,2,5-f'-5* of methane proton H^5 is equal to [(+170) – (+250)] = **-80 mlrd**.

We can conclude that introduction of third methyl group at C-5 to the existing two methyl substituents at the carbon atom C-2 in 2,2,5-trimethylalkanes **2,2,5-n** has no effect on ***BSP*** nonaprotonic singlet signal of methyl protons H-1 , H-2 ' and H-2 " (tert-butyl protons).

On the other hand the presence of the above pentacarbonic fragment $\{[C^1H^1{}_3-C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)–C^3H^3{}_2-]\}$ instead of propyl tricarbonic moiety $\{[C^1H^1{}_3-C^2H^2{}_2–C^3H^3{}_2-]\}$ in 5-monomethylyexane (**5n** in reverse numbering) has only a small effect on the ***BSP*** hexaprotonic doublet signal value of methyl protons H-5' and H-6 in 2,2,5-trimethylhexane **2,2,5-f**. However we want to emphasize that methine proton H-5 ***DSP*** value in 2,2,5-trimethylhexane **2,2,5-f** (***2,2,5-f-5* = +170 mlrd.**) significantly shifted upfield compared to "standard "mean differential parameters in abovementioned 2-methyalkanes 2n (***2n-2* = +250 mlrd.**), ie, the "additional" differential parameter *2,2,5-f'-5* is equal to = **-80 mlrd**.

We now calculate the values of "integral spectral changes" **Σ(N^1,N^2,N^3-*f-i*)** for two of the aforementioned virtual transitions: a) **2,2-n → 2,2,5-f** and b) **2-n → 2,2,5-f**. If not discuss the changes of four protons H-3 and H-4 and take the zero change of nonaprotonic singlet signal of methyl protons H-1, H-2 'and H-2" (as mentioned above), then the values of "integral spectral changes" **Σ(N^1,N^2,N^3-*f-i*)** are almost equals the sum of: 6 x (+15) + (-80) = 90 -80 = **+ 10 mlrd**.

If, after all, take into consideration the formal values of changes protons H-3 and H-4 parameter, equal to -100 **mlrd.** (calculation of which is omitted here), then the values of "integral spectral changes" **Σ(N^1,N^2,N^3-*f-i*)** will be equal to: (+10) + (-100) = **-90 mlrd**.

Given the fact that we considered just only one example of 2,2,5-trimethylalkanes **2,2,5-n** – ie, 2,2,5-trimethylhexane **2,2,5-f**, to the subsequent conclusions we treat with caution. Thus, it is ***possible to draw a cautious conclusion***: when the molecule of 2,2,5-trimethylhexane **2,2,5-f** ***build of two virtual parts***: the pentacarbonic fragment $\{[C^1H^1{}_3-C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)–C^3H^3{}_2-]\}$ (11 protons) and the tetracarbonic fragment $\{[-C^4H^4{}_2-C^5H^5(C^{5'}H^{5'}{}_3)–C^6H^6{}_3]]\}$ (9 protons), ***the integral value*** of the ***BSP*** parameters of all 20 protons in **2,2,5-f** (**Σ(N^1,N^2,N^3-*f-i*)**) is **or practically unchanged** (unless you consider 4 protons H-3 and H-4) **or not significantly shift upfield** (if the formal accounting of protons H-3 and H-4).

So for a family of 2,2,5-trimethylalkanes **2,2,5-n** represented by a single substance **2,2,5-f** we observe, as expected the almost complete lack of influence to the abovementioned two fragments each other.

3.1.1.2. Calculations of “aggregated” spectral parameter Σ *2,2,5-f-i*.

Let’s consider now integral parameter - the “aggregated” spectral changes denoted as **Σ *N^1,N^2,N^3-n-i*** (see [2]) for only representative of 2,2,5-trimethylalkane **2,2,5-n** family - 2,2,5-trimethylhexane **2,2,5-f,** ie, **Σ *2,2,5-f-i***.

Let’s calculate the “aggregated” spectral changes **Σ *2,2,5-f-i*** of 2,2,5-trimethylhexane **2,2,5-f** as the sum of "standard" differential parameters ***2,2,5-f-i***, given in parts 3.1.1. (***2,2,5-f-1* = *2,2,5-f-2’* = *2,2,5-f-2’’* = -18**; ***2,2,5-f-3*** = ***2,2,5-f-4* = -130**; ***2,2,5-f-5* = +170**; ***2,2,5-f-5’* = *2,2,5-f-6* = 0**). The “aggregated” spectral changes **Σ *2,2,5-f-i*** for 20 protons are: [9 x (- 18)] + [2 x (-130)] + [2 x (-130)] + [1 x (+170)] + [6 x (0)] = (-162 -260 -260 +170 +0) = **-512 (≈ +510 mlrd.)**. So this rounded sum is equal to: **-510 mlrd.**

As was said above the compound **2,2,5-f** consists of two part:s the “pentacarbonic fragment” **$[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}C^3H^3_2\text{-}]$** and tetracarbonic fragments **$[\text{-}C^4H^4_2\text{-}C^5H^5(C^{5'}H^{5'}_3)\text{–}C^6H^6_3]$**, which do **not overlap one another**, but **“touching each other”**. So on the other hand we can estimate the “aggregated” spectral change **Σ *2,2,5-f-i*** of 2,2,5-trimethylhexane **2,2,5-f** as the sum of two terms: **Σ *2,2-n-i*** (for“pentacarbonic fragment” **$[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}C^3H^3_2\text{-}]$**) and **Σ *2n-i*** (for tetracarbonic fragments **$[\text{-}C^4H^4_2\text{-}C^5H^5(C^{5'}H^{5'}_3)\text{–}C^6H^6_3]$**). Parameter **Σ *2,2-n-i*** for 11 protons (***2,2-n-1* = -20**; ***2,2-n-3* = -100**; and: ***2,2-n-2’* = -20**, ***2,2-n-2’’* = -20**) is equal to [2]: [9 x (-20)] + +[2 x (-100)] =(-180-200) = **-360.** Parameter **Σ *2n-i*** for 9 protons (***2n-1* = -15**; ***2n-2* = +250**; ***2n-3* = -110** and: ***2,2-n-2’* = -15**) is equal to [2]: [6 x (-15)] +[1 x (+250)] +[2 x (-110)] =(-90 + 250 -220) = **-60.**

So this sum is equal to: (-360) + (-60) = **-420 mlrd.**

When comparing the two calculations shows that they are fairly close values (**-420** versus **-510**). The resulting difference (90 **mlrd.**) we explain the use of different values of ***2,2,5-f-3*** and ***2,2,5-f-4*** parameters (-130 versus -110 **mlrd.**). Many spectral parameters of methylene protons, including the abovementioned, are not in our opinion quite rigorous justification. Therefore, the differences of these parameters are possible, and it is how we can explain the possible difference between the two calculated values.

Now we consider possible ways of hexane **f** converting into 2,2,5-trimethylhexane **2,2,5-f** through the forming of 2-methylhexane **2f** and 2,N-dimethylhexane **2,N^2–f**. There are two ways of said conversion. This three-stage process generally designated as **f → 2f → 2,N^2–f → 2,2,5-f**.

In the first way hexane **f** converts into 2,2,5-trimethylhexane **2,2,5-f** through the forming of 2-methylhexane **2f** and than through 2,2-dimethylhexane **2,2-f** in the second stage (**2f → 2,2-f**, ie, **N^2 = 2** and **2,N^2–f = 2,2-f**). The two first stages summary "integral spectral changes" **Σ *2,2-n-i*** as indicated above is equal to **-360 mlrd.** The third stage of the whole pathway (the **introduction of a third methyl group CH_3** into dimethylhexane **N^1N^2–f,** ie, the transformation **2,2-f → 2,2,5-f**) leads to only a slight change of the “aggregated”parameter on value by **-60 mlrd.** This figure is numerically equal the abovementioned “aggregated”parameter **Σ *2n-i***. So the “aggregated” parameter of transition **Σ *2,2-f-i* → Σ *2,2,5-f-i*** in the third stage of whole process, ie, **2,2-f → 2,2,5-f** is numerically equal the abovementioned “aggregated”parameter of transition **f → 2f** in the first stage of whole process.

In the second way hexane **f** converts into 2,2,5-trimethylhexane **2,2,5-f** through the forming of 2-methylhexane **2f** and through the 2,5-dimethylhexane **2,5-f** (**f → 2f → 2,5-f → 2,2,5-f** ie, **N^2 = 5** and **2,N^2–f = 2,5-f**). It is interesting that the calculation of the “aggregated” parameter **Σ *2,5-f-i*** at the process of two methyl groups introducing in 2- and 5-positions in hexane **f** (i.e. in the **f → 2,5-f** process) gives a value of **Σ *2,5-f-i*** equal to **-125 mlrd.** This value is equal to twice the amount the abovementioned “aggregated”parameter **Σ *2n-i***, and more than three times less than the “aggregated” parameter **Σ *2,2,5-f-i*** (**-420 mlrd.**). So using this approach, we can say, that the third stage of the whole pathway (ie, the **introduction of a third methyl group CH_3** to atom C-2 instead hydrogen atom H-2) in 2,5-dimethylhexane **2,5-f** when it the convert into 2,5-trimethylhexane **2,2,5-f** results in a change of the “aggregated” parameter on value by **-300 mlrd.** (ie transition **Σ *2,5-f-i* → Σ *2,2,5-f-i*** in process **2,5-f → 2,2,5-f**).

So it’s interesting to compare two “aggregated”parameters of two different third stages of the whole pathway **f → 2,2,5-f**. The parameter of transition **2,2-f → 2,2,5-f** (**-60 mlrd.**) is less than 5 times the absolute magnitude of the parameter of transition **2,5-f → 2,2,5-f** (**-300 mlrd.**) Comparing both abovementioned transition ways (**f → 2f → 2,N^{2}–f → 2,2,5-f**) from hexane **f** to trimethylhexane **2,2,5-f**, we can **conclude about the importance of the number (position) of carbon atoms N^{3} in the molecule** of hexane **f**, which introduces the third methyl group.

It can be assumed that the introduction of an additional methyl group in β-position of a long chain alkane (*2-position of hexane **f** in first stage of first way* or into *5-position of 2,2-dimethylhexane **2,2-f** in third stage of second way*) leads in both cases to same value of the stage "aggregated" parameter, which is equal to **-60 mlrd.** And the introduction of an additional methyl group in 2-position of a long chain 2-methylalkane (into *2-position of monomethylhexane **2f** in second stage of first way* or into *2-position of 2,5-dimethylhexane **2,5-f** in third stage of second way*) leads in both cases to same value of the stage "aggregated" parameter to 5 times greater than the previous, which is equal to **-300 mlrd.**

Thus every the three-stage process **f → 2f → 2,N^{2}–f → 2,2,5-f** "aggregated" parameter **Σ *2,2,5-f-i*** when both paths transition from **f** to **2,2,5-f** includes two terms of (**-60 mlrd.**) **and one term** of (**-300 mlrd.**). So the total value of the "aggregated" parameter **Σ *2,2,5-f-i***in both cases equal to **-420 mlrd.**

3. 1. 2. The Family of 2,2,4-trimethylalkanes (2,2,4-n).

In the family of 2,2,4-trimethylalkanes **2,2,4-n** of the general formula: $\mathbf{C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{-}C^{5}H^{5}_{2}}\text{–}\ldots\text{-}C^{n-1}H^{n-1}_{2}\text{-}C^{n}H^{n}_{3}$ the carbon atoms in which there are branching (C-2 and C-4), are separated by only one methylene groups **($-C^{3}H^{3}_{2}-$)**. Therefore, the most interesting to us are the abovementioned "pentacarbonic fragment" **[$C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}C^{3}H^{3}_{2}\text{-}$]** and tetracarbonic fragments **[$\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{–}C^{5}H^{5}_{2}\text{-}$]** and as a consequence of it – octacarbonic fragment **[$C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{–}C^{5}H^{5}_{2}\text{-}$].** Both abovementioned fragments (C-1 –C-3) and (C-3 –C-5) we are interested in **overlap one another**, so far as **they have a common methylene group $\text{–}C^{3}H^{3}_{2}\text{-}$.** Therefore, as in the case of 2,4-dimethylalkanes **2,4-n**, for the family of 2,2,4-trimethylalkanes **2,2,4-n** we can expected the mutual influence of two closely spaced methyl groups (at C-2 and C-4) on the ***BSP*** values of octacarbonic molecule fragment C-1 –C-5, especially on the protons H-3.

In the sources we use are given spectral data of two representatives of the of 2,2,4-trimethylalkanes **2,2,4-n** family: 2,2,4-trimethylpentane **2,2,4-e** and 2,2,4-trimethylhexane **2,2,4-f**. The first of them - 2,2,4-trimethylpentane **2,2,4-e** - we are considering, according to previously accepted definitions [1, 2] as shortchain alkane (because branching at the distal end of the longest chain, i.e., at C-4 is disposed at the β-carbon atom); the second - 2,2,4-trimethylhexane **2,2,4-f** – as midchain alkane (because branching at the distal end of the longest chain, i.e., at C-4 is disposed at the γ-carbon atom).

For the first substance - **2,2,4-e** – the protonic spectral data are present in both sources [3,4], and they are consistent with each other. So we'll discuss the details of data [3], as they are presented with greater accuracy, ie to 0.001 ppm (1 **mlrd.**). For the second substance - **2,2,4-f** - data are present in only sources [3] with accuracy to 0.001 ppm (1 **mlrd.**) also. We emphasize once again, that the spectrum of **2,2,4-f** was obtained at a low frequency instrument (90 MHz) ie, with less accuracy.

In molecule of both studied 2,2,4-trimethylalkanes **2,2,4-n** the values of base ***2,2,4-n-B-i*** (in **ppm**) and the "standard" differential parameters ***2,2,4-n-i*** (in **mlrd.**) are equal to:

2,2,4-trimethylpentane **2,2,4-e:** ***2,2,4-e-B-1*** = ***2,2,4-e- B-2'*** = ***2,2,4-e-B-2''*** = 0.892, ***2,2,4-e-1* = *2,2,4-e-2'* = *2,2,4-e-2''* = +12**; ***2,2,4-e-B-3*** = 1.122; ***2,2,4-e-3* = -148**; ***2,2,4-e-B-4*** = 1.657; ***2,2,4-e-4* = +387**; ***2,2,4-e-B-4'*** = ***2,2,4-e-B-5*** = 0.907; ***2,2,4-e-4'* = *2,2,4-e-5* = +27**.

2,2,5-trimethylhexane **2,2,5-f:** ***2,2,4-f-B-1*** = ***2,2,4-f-B-2'*** = ***2,2,4-f-B-2''*** = 0.887, ***2,2,4-f-1* = *2,2,4-f-2'* = *2,2,4-f-2''* = +7**; ***2,2,4-f-B-3A*** = 1.014; ***2,2,4-f-3A* = -256**; ***2,2,4-f-B-3B*** = 1.207; ***2,2,4-f-3B* = -63;** ***2,2,4-f-B-4*** = 1.35; ***2,2,4-f-4* = +80**; ***2,2,4-f-B-4'*** = 0.896; ***2,2,4-f-4'* = +16**; ***2,2,4-f-B-5A*** = 1.15; ***2,2,4-f-5A* = -120**; ***2,2,4-f-B-5B*** = 1.29; ***2,2,4-f-5B* = +20;** ***2,2,4-f-B-6*** = 0.853; ***2,2,4-f-6* = -27**.

As said above in the studied spectra of 2,2,4-trimethylalkanes **2,2,4-n** family we considered the **"octacarbonic" fragment [$C^{1}H^{1}_{3}\text{-}C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})\text{–}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{–}C^{5}H^{5}_{2}\text{-}$]** as the whole **moiety that forming the spectral changes** from the spectrum of the linear alkane. Therefore, the most logical to compare its spectral parameters with the same spectral parameters of **"heptacarbonic" fragment [$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{–}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})\text{–}C^{5}H^{5}_{2}\text{-}$]** as the whole **moiety** in 2,4-dimethylalkanes **2,4-n**.

Then, on the one hand it seems appropriate to compare the “pentacarbonic fragment” **$[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}_{2}-]$** in 2,2,4-trimethylalkanes **2,2,4-n** with the similar “pentacarbonic fragments” **$[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}_{2}-]$** in 2,2,5-trimethylalkanes (**2,2,5-n = 2,2,5-f**), discussed above and with the same moiety in 2,2-dimethylalkanes **2,2-n**, discussed earlier [2].

On the other hand tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,2,4-trimethylpentane **2,2,4-e** it seems appropriate to compare with three similar tetracarbonic fragments in other methylalkanes families. Firstly with the tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,4-dimethylpentane **2,4-e**, discussed previously [2]. Secondly, with the aforementioned tetracarbonic fragments **$[-C^{4}H^{4}_{2}-C^{5}H^{5}(C^{5'}H^{5'}_{3})–C^{6}H^{6}_{3}]$** in 2,2,5-trimethylalkanes **2,2,5-f**, discussed above. And finally, with the tetracarbonic fragment **$[C^{1}H^{1}_{3}-C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}_{2}-]$** in family of mono-2-methylalkanes **2n** [2].

The same applies to pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,2,4-trimethylhexane **2,2,4-f.** It seems appropriate to compare it with the pentacarbonic fragments **$[C^{1}H^{1}_{3}-C^{2}H^{2}_{2}-C^{3}H(C^{3'}H^{3'}_{3})–C^{4}H^{4}_{2}-]$** in family of mono-3-methylalkanes **3n** previously discussed in [1].

3.1.2.1. Calculations of "additional" mean differential parameters *2,2,4-n'-1.*

So the first "additional" mean differential parameters designated as ***2,2,4-n'-1*** (***2,2,4-n'-1 = 2,2,4-n'-2' = 2,2,4-n'-2''***) we calculated as the difference between the "standard" mean differential ***2,2,4-n-1*** in 2,2,4-trimethylalkanes **2,2,4-n** (2,2,4-trimethylpentane **2,2,4-e** and 2,2,4-trimethylhexane **2,2,4-f**) and "standard" mean differential parameters ***2,2,5-n-1*** in abovementioned 2,2,5-trimethyalkanes **2,2,5-n.** The "standard" mean differential parameters ***2,2,5-n-1*** in 2,2,5-dimethyalkanes **2,2,5-n** we take equal the parameter of the only family representative 2,2,5-dimethylhexane, ie ***2,2,5-n-1 = 2,2,5-f-1 = -18*** (rounded to **-20 mlrd.**). The "standard" mean differential parameters ***2,2,4-n-1*** we calculated as the arithmetic mean between "standard" differential parameters ***2,2,4-e-1*** = +12 and ***2,2,4-f-1***= +7. So, ***2,2,4-n-1*** = +12 + 7 / 2 ≈ **+10 mlrd.** Hence the calculated first "additional" "rounded" differential parameter ***2,2,4-n'-1*** is equal to: ***2,2,4-n-1 - 2,2,5-n-1*** = [(+10) – (-20] ≈ **+30 mlrd.**

The second "additional" mean differential parameters designated ***2,2,4-n''-1*** we again calculated as the difference between the "standard" mean differential parameter ***2,2,4-n-1*** in 2,2,4-trimethylalkanes (**+10 mlrd.**) and "standard" mean differential parameters ***2,2-n-1*** in 2,2-dimethyalkanes **2,2-n** (***2,2-n-1= -20mlrd.***, see above**).** Hence the calculated second "additional" "rounded" differential parameter ***2,2,4-n''-1*** is equal to: ***2,2,4-n-1 - 2,2-n-1*** = [(+10) – (-20] ≈ **+30 mlrd.** This second "additional" mean differential parameters designated ***2,2,4-n''-1*** we can compute by another method also. You need to add the abovementioned first "additional" mean differential parameters designated ***2,2,4-n'-1*** with the "additional" differential parameters ***2,2,5-n'-1*** discussed above {(***2,2,4-n-1 - 2,2,5-n-1***) + (***2,2,5-n-1 - 2,2-n-1***) = ***2,2,4-n-1 - 2,2-n-1***}: [(+30) + 0] = **+30 mlrd.** This second method of the "additional" differential parameters calculation, we will use in the future.

Thus, both types of calculations yield the same value of "additional" mean differential parameters ***2,2,4-n'-1***, equal to +30 **mlrd.**

3.1.2.2. Calculations of "additional" mean differential parameters *2,2,4-n'-3.*

On the one hand, the methylene group $-C^{3}H^{3}_{2}-$ is the central moiety in the octacarbonic fragment **$[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}-]$** of 2,2,4-trimethylalkanes **2,2,4-n**. Therefore, the most logical to compare its spectral parameters with the same spectral parameters of $-C^{3}H^{3}_{2}-$ group in 2,4-dimethylalkanes **2,4-n**. In this way we calculated the first "additional" differential parameters designated as ***2,2,4-n'-3***.

On the other hand protons H-3 in $-C^{3}H^{3}_{2}-$ group in 2,2,4-trimethylalkanes **2,2,4-n** as stated above are present simultaneously in “pentacarbonic fragment” **$[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}_{2}-]$** and in: a) tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,2,4-trimethylpentane **2,2,4-e**; or b) in pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,2,4-trimethylhexane **2,2,4-f**. So we also discuss next two "additional" differential parameters (second and third) designated as ***2,2,4-n''-3*** and ***2,2,4-***

n'''-3 respectively (vide infra). Let's calculate separately all three "additional" differential parameters (***2,2,4-n'-3***, ***2,2,4-n''-3*** and ***2,2,4-n'''-3***) separately for each of the two members of the family 2,2,4-trimethylalkanes **2,2,4-n.**

2,2,4-trimethylpentane **2,2,4-e**. The first "additional" mean differential parameters ***2,2,4-e'-3*** as stated above we calculated as the difference between the "standard" differential ***2,2,4-e-3*** (**-148 mlrd.**) in 2,2,4-trimethylpentane **2,2,4-e** and discussed previously [2] "standard" differential parameter ***2,4-e-3*** (**-240 mlrd.**) in 2,4-dimethylpentane **2,4-e**. So, ***2,2,4-e-3'*** = (**-148**) – (**-240**) = **+ 92** ≈ **+90 mlrd.**

The second "additional" differential parameters ***2,2,4-e''-3*** we calculated as the difference between the "standard" differential parameter ***2,2,4-e-3*** (**-148 mlrd.**) in 2,2,4-trimethylpentane **2,2,4-e** and "standard" mean differential parameter ***2,2-n-3*** (**-100 mlrd.**, see above) in the family of 2,2-dimethylalkanes **2,2-n**, discussed earlier. So, ***2,2,4-e-3''*** = (**-148**) – (**-100**) = **-48 mlrd.** (≈ **-50 mlrd.**).

And finally, the third "additional" mean differential parameters ***2,2,4-e'''-3*** as stated above we calculated as the difference between the "standard" differential parameter ***2,2,4-e-3*** (**-148 mlrd.**) in 2,2,4-trimethylpentane **2,2,4-e** and "standard" differential parameter ***2n-3*** (**-110 mlrd.** [1]) in 2-monomethylpentane family **2e**, discussed previously [1]. So, ***2,2,4-e-3'''*** = (-148) – (-110) = **-38 mlrd.** (≈ **-40 mlrd.**).

2,2,4-trimethylhexane **2,2,4-f.** Then we calculate and discuss two "additional" differential parameters of 2,2,4-trimethylhexane **2,2,4-f**, designated as ***2,2,4-f'-3*** and ***2,2,4-f'''-3*** (the second "additional" differential parameter ***2,2,4-f''-3*** of 2,2,4-trimethylhexane **2,2,4-f** is approximately the same as for calculated above parameters ***2,2,4-e-3''*** ≈ **-50 mlrd.** of 2,2,4-trimethylpentane **2,2,4-e**).

Both protons H-3 of the methylene groups -$C^3H^3_2$- give multiplet signals in spectrum of unsymmetrical 2,2,4-dimethylhexane **2,2,4-f** (as in the case of discussed earlier [2] 2,4-dimethylhexane **2,4-f**) which are magnetically nonequivalent and are equal to: ***2,2,4-f-B-3A*** = 1.014 ppм, ***2,2,4-f-B-3B*** = 1.207 ppм. (calculated "aggregated" parameter ***2,2,4-f-B-3*** = 1.111 ppm; compare with ***2,2,4-e-B-3*** = 1.122 ppm). Therefore it seems appropriate to consider separately each of the 3 basic parameters: ***2,2,4-f-B-3A***, ***2,2,4-f-B-3B*** and "aggregated" parameter ***2,2,4-f-B-3*** and calculate for each of them two "additional" differential parameters, which are described above.

The first "additional" differential parameters ***2,2,4-f'-3A*** we calculate as the difference between the "standard" differential highfield proton's parameter in 2,2,4-trimethylhexane **2,2,4-f** [***2,2,4-f-3A*** (**-256 mlrd.**)] and similar "standard" differential parameter ***2,4-f-3A*** (**-300 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**, discussed previously [2]. Hence the calculated first "additional" differential parameter ***2,2,4-f'-3A*** for highfield proton is equal to: ***2,2,4-f-3A - 2,4-f-3A*** = [(-256) – (-300] = **+44 mlrd.** (≈ **+45 mlrd.**). Similarly the first "additional" differential parameters ***2,2,4-f'-3B*** for downfield proton is calculated as the difference between ***2,2,4-f-3B*** (**-63 mlrd.**) and ***2,4-f-3B*** (**-160 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**. Hence first "additional" downfield differential parameter ***2,2,4-f'-3B*** is equal to: [(-63) – (-160] = **+97 mlrd.** (≈ **+95 mlrd.**). Similarly the first "additional" "aggregated" differential parameters ***2,2,4-f'-3*** is calculated as the difference between ***2,2,4-f-3*** [ie = [(-256) + (-63)] / 2 ≈ **-160 mlrd.**) and ***2,4-f-3*** (**-230 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**. Hence ***2,2,4-f'-3*** is equal to: [(-160) – (-230] = **+71 mlrd.** (or by another method of calculations: [(+44) + (-97)] / 2 = **+71 mlrd.**) ≈ **+70 mlrd.**].

And finally, the corresponding third "additional" differential parameters designated as "***2,2,4-f'''-3***" as stated above we calculated as the difference between the corresponding "standard" differential parameters in 2,2,4-trimethylhexane **2,2,4-f** and "standard" differential parameters (***3f-4A*** = -190 **mlrd.**, ***3f-4B*** = +10 **mlrd.**, and ***3f-4***= -90 **mlrd.** [1]) in 3-monomethylhexane **3f**, discussed previously [1]. So, the third "additional" highfield differential parameter ***2,2,4-f'''-3A*** = [(-256) – (-190] = **-66 mlrd.** (≈ **-65 mlrd.**). The third "additional" downfield differential parameter ***2,2,4-f'''-3B*** = [(-63) – (+10] = **-73 mlrd.** (≈ **-75 mlrd.**). And the third "additional" "aggregated" differential parameter ***2,2,4-f'''-3*** = [(-159) – (-90] = **-69.5 mlrd.** (≈ **-70 mlrd.**) or [(-66) + (-73) / 2] ≈ **-70 mlrd.**

Now let's calculate the arithmetic mean parameters for the entire family of 2,2,4-trimethylalkanes **2,2,4-n** as half the sum of the corresponding parameters ***2,2,4-e-3*** and ***2,2,4-f-3***. Since two protons H-3 in 2,2,4-trimethyl pentane **2,2,4-e** are magnetically equivalent it seems appropriate to discuss only the "additional" "aggregated" differential parameters. So, the first "additional" mean "aggregated" differential parameter ***2,2,4-n'-3*** is equal to [= +90 + 70 / 2] = **+80 mlrd.** The second "additional" mean differential parameter ***2,2,4-n-3''*** as mentioned above is equal to [***2,2,4-e-3''*** ≈ ***2,2,4-f''-3***] = **-50 mlrd.** And the third "additional" mean "aggregated" differential parameter ***2,2,4-n'''-3*** is equal to [= (-40) + (-70) / 2] = **-55 mlrd.**

Thus, it is ***possible to draw two cautious conclusions***: 1) introduction of an additional methyl group instead of a hydrogen atom H-2 in 2,4-dimethylalkanes **2,4-n** with transition to 2,2,4-trimethylalkanes **2,2,4-n** leads to a **downfield shift** of the arithmetic mean both basic basic (***2,2,4-n-B-3***) and first "additional" mean "aggregated" differential parameter ***2,2,4-n'-3*** of two H-3 protons.

2) However, if both molecules of 2,2,4-trimethylalkane family (**2,2,4-e** and **2,2,4-f**) are regarded as an amount of two parts (with **$-C^{3}H^{3}_{2}-$** group in each part) {ie the pentacarbonic fragment **$[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}_{2}-]$** and the tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}-]$**}, then it can be said the following. At the both transitions [1) **2,2-n** → **2,2,4-n** and 2) **Nn** → **2,2,4-n**, where **N** = 2 or 3, see above] we observe a **highfield shift** of the arithmetic mean both basic (***2,2,4-n-B-3***), second (***2,2,4-n''-3***) and third (***2,2,4-n'''-3***) "additional" mean "aggregated" differential parameters for each two protons H-3 of fragment **$-C^{3}H^{3}_{2}-$**.

3.1.2.3. Calculations of "additional" mean differential parameters *2,2,4-n'-4.*

The considered methyne proton H-4 enters into tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}-$** of each molecule of 2,2,4-trimethylalkane family (**2,2,4-e** and **2,2,4-f**). So the tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,2,4-trimethylpentane **2,2,4-e** it seems appropriate to compare with similar tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,4-dimethylpentane **2,4-e**, discussed previously [2]. The same applies to pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,2,4-trimethylhexane **2,2,4-f.** It also seems appropriate to compare it with the pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,4-dimethylhexane **2,4-f** [2].

The "additional" differential parameters ***2,2,4-e'-4*** we calculate as the difference between the "standard" differential parameter in 2,2,4-trimethylpentane **2,2,4-e** [***2,2,4-e-4*** (**+387 mlrd.**)] and similar "standard" differential parameter ***2,4-e-4*** **= +349 mlrd.** [2]) in 2,4-dimethylpentane **2,4-e**, discussed previously [2]. Hence the calculated "additional" differential parameter ***2,2,4-e'-4*** for methyne proton H-4 is equal to: ***2,2,4-e-4 - 2,4-e-4*** = [(+387) – (+349] = **+38 mlrd.** (≈ **+40 mlrd.**).

The "additional" differential parameters ***2,2,4-f'-4*** we calculate as the difference between the "standard" differential parameter [***2,2,4-f-4*** (**+80 mlrd.**)] in 2,2,4-trimethylhexane **2,2,4-f** and similar "standard" differential parameter ***2,4-f-4*** (**+110 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**, discussed previously [2]. Hence the calculated "additional" differential parameter ***2,2,4-f'-4*** for methyne proton H-4 is equal to: ***2,2,4-f-4 - 2,4-f-4*** = [(+80) – (+110] = **-30 mlrd.**

Now let's calculate the arithmetic mean parameters ***2,2,4-n'-4*** for the entire family of 2,2,4-trimethylalkanes **2,2,4-n** as half the sum of the corresponding parameters ***2,2,4-e'-4*** and ***2,2,4-f'-4***. "Additional" mean differential parameter ***2,2,4-n'-4*** is equal to [= (+40) + (-30) / 2] = **+5 mlrd.**

Thus, it is ***possible to draw a cautious conclusions***: An introduction of an additional methyl group instead of a hydrogen atom H-2 in 2,4-dimethylalkanes **2,4-n** with transition to 2,2,4-trimethylalkanes **2,2,4-n** leads to a small in magnitude, but multidirectional sign "additional" mean differential parameter ***2,2,4-n'-4*** of H-4 methyne proton in 2,2,4-trimethylpentane **2,2,4-e** and 2,2,4-trimethylhexane **2,2,4-f**._"Additional" mean differential parameter ***2,2,4-n'-4*** is close to zero.

3.1.2.4. Calculations of "additional" mean differential parameters *2,2,4-n'-4'.*

The considered three methyl protons H-4' enters into pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,2,4-trimethylhexane **2,2,4-f.** On the other hand, six magnetically equivalent protons (three H-4' protons in $–C^{4'}H^{4'}_{3}$ group and three H-5 protons in $–C^{5}H^{5}_{3}$ group) are present in the tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$** in 2,2,4-trimethylpentane **2,2,4-e.**

So the pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,2,4-trimethylhexane **2,2,4-f** it seems appropriate to compare with similar pentacarbonic fragments **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{2}–C^{6}H^{6}_{3}]$** in 2,4-dimethylhexane **2,4-f.** And the same applies to tetracarbonic fragment **$[-C^{3}H^{3}_{2}-C^{4}H^{4}(C^{4'}H^{4'}_{3})–$**

$C^{5}H^{5}{}_{3}$] in 2,2,4-trimethylpentane **2,2,4-e** which we compare with similar tetracarbonic fragment **[-$C^{3}H^{3}{}_{2}$-$C^{4}H^{4}(C^{4'}H^{4'}{}_{3})$–$C^{5}H^{5}{}_{3}$]** in 2,4-dimethylpentane **2,4-e**, discussed previously [2].

The "additional" differential parameters ***2,2,4-f'-4'*** of three methyl protons H-4' in 2,2,4-trimethylhexane **2,2,4-f** we calculate as the difference between the "standard" differential parameter [***2,2,4-f-4'*** (**+16 mlrd.**)] in 2,2,4-trimethylhexane **2,2,4-f** and similar "standard" differential parameter ***2,4-f-4'*** (**-55 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**, discussed previously [2]. Hence the calculated "additional" differential parameter ***2,2,4-f'-4'*** for three methyl protons H-4' is equal to: ***2,2,4-f-4' - 2,4-f-4'*** = [(+16) – (-55] = +71 **mlrd.** (≈ **+70 mlrd.**).

The "additional" differential parameters ***2,2,4-e'-4'*** of six methyl protons H-4' and H-5 in 2,2,4-trimethylpentane **2,2,4-e** we calculate as the difference between the "standard" differential parameter in 2,2,4-trimethylpentane **2,2,4-e** [***2,2,4-e-4'*** (**+27 mlrd.**)] and similar "standard" differential parameter ***2,4-e-4'*** (***2,4-e-4' = 2,4-e-2' = 2,4-e-1 = 2,4-e-5* = -30 mlrd.** [2]) in 2,4-dimethylpentane **2,4-e**, discussed previously [2]. Hence the calculated "additional" differential parameter *2,2,4-e'-4* for 6 methyl protons H-4' and H-5 is equal to: ***2,2,4-e-4' - 2,4-e-4'*** = [(+27) – (-30] = +57 **mlrd.** (≈ **+55 mlrd.**).

Now let's calculate the arithmetic mean parameters ***2,2,4-n'-4'*** for the entire family of 2,2,4-trimethylalkanes **2,2,4-n** as half the sum of the corresponding parameters ***2,2,4-e'-4'*** and ***2,2,4-f'-4'***. "Additional" mean differential parameter ***2,2,4-n'-4'*** is equal to [= (+71) + (+57) / 2] = +64 **mlrd.** (≈ **+65 mlrd.**).

Thus, it is ***possible to draw a cautious conclusions***: An introduction of an additional methyl group instead of a hydrogen atom H-2 in 2,4-dimethylalkanes **2,4-n** with transition to 2,2,4-trimethylalkanes **2,2,4-n** leads to a large in magnitude and positive by sign "additional" mean differential parameter ***2,2,4-n'-4'*** of three H-4' methyne protons in 2,2,4-trimethylpentane **2,2,4-e** and six methyne protons (three H-4' and three H-5) in 2,2,4-trimethylhexane **2,2,4-f** (***2,2,4-n'-4'*** ≈ **+65 mlrd.**).

3.1.2.5. Calculations of "additional" differential parameters *2,2,4-f'-5* in 2,2,4-trimethylhexane 2,2,4-f.

Let's consider the last methylene group **–$C^{5}H^{5}{}_{2}$–** in the octacarbonic fragment **[$C^{1}H^{1}{}_{3}$-$C^{2}(C^{2'}H^{2'}{}_{3})(C^{2''}H^{2''}{}_{3})$–$C^{3}H^{3}{}_{2}$-$C^{4}H^{4}(C^{4'}H^{4'}{}_{3})$–$C^{5}H^{5}{}_{2}$-]** of 2,2,4-trimethylhexane **2,2,4-f** (methyl group **–$C^{6}H^{6}{}_{3}$** in this fragment does not go). The "additional" "aggregated" differential parameters ***2,2,4-f'-5*** of two magnetically nonequivalent methylene protons H-5 in 2,2,4-trimethylhexane **2,2,4-f** we calculate as the difference between the "standard" differential parameter {***2,2,4-f-5*** [(-120) + (+20) / 2 = **-50 mlrd.**)] in 2,2,4-trimethylhexane **2,2,4-f** and similar "standard" differential parameter ***2,4-f-5*** (**-60 mlrd.** [2]) in 2,4-dimethylhexane **2,4-f**, discussed previously [2]. Hence the calculated "additional" differential parameter ***2,2,4-f'-5*** for two methylene protons H-5 is equal to: ***2,2,4-f-5 - 2,4-f-5*** = [(-50) – (-60)] = +10 **mlrd.**

Thus, it is ***possible to draw a cautious conclusions***: An introduction of an additional methyl group instead of a hydrogen atom H-2 in 2,4-dimethylhexane **2,4-f** with transition to 2,2,4-trimethylhexane **2,2,4-f** leads to a small in magnitude and positive by sign "additional" mean differential parameter ***2,2,4-f'-5*** of two H-5 methylene protons in 2,2,4-trimethylhexane **2,2,4-f**. So this "additional" "aggregated" differential parameter ***2,2,4-f'-5*** is close to zero, ie, the transition **2,4-f** → **2,2,4-f** practically no effect on the two H-5 methylene protons absorption.

3.1.2.6. Calculations of the "aggregated" spectral changes (parameter Σ *2,2,4-n-i*) of the 2,2,4-trimethylalkanes family 2,2,4-n.

As shown above, the "aggregated" (integral) spectral changes denoted as **Σ *N^{1},N^{2},N^{3}-n-i*** (see [2]) in the case of the 2,2,4-trimethylalkanes family **2,2,4-n** referred to as **Σ *2,2,4-n-i***.

It is the sum of changes in all the spectral parameters that occurred during the conversion from linear alkanes **n** to the families of **2,2,4-n** trimethylalkanes relatively to the abovementioned octacarbonic **[$C^{1}H^{1}{}_{3}$-$C^{2}(C^{2'}H^{2'}{}_{3})(C^{2''}H^{2''}{}_{3})$–$C^{3}H^{3}{}_{2}$-$C^{4}H^{4}(C^{4'}H^{4'}{}_{3})$–$C^{5}H^{5}{}_{2}$-]** moiety. We calculate this parameter separately for each of the two members of the **2,2,4-n** trimethylalkanes family. All required values of the "standard" differential spectral parameters ***2,2,4-n-i*** are given in parts 2.1.2.

2,2,4-trimethylpentane **2,2,4-e.** (***2,2,4-e-1 = 2,2,4-e-2' = 2,2,4-e-2'' = +12***; ***2,2,4-e-3 = -148***; ***2,2,4-e-4* = +387**; ***2,2,4-e-4' = 2,2,4-e-5* = +27**). So the "aggregated" spectral changes **Σ *2,2,4-e-i*** for 17 protons are: [9 x (+12)] + [2 x (-148)] + [1 x (+387)] + [5 x (+27)] = (+108 -296 +387 +135) = **+334** (≈ **+335 mlrd.**).

2,2,4-trimethylhexane **2,2,4-f.** (***2,2,4-f-1 = 2,2,4-f-2' = 2,2,4-f-2'' = +7***; ***2,2,4-f-3A = -256***; ***2,2,4-f-3B* = -63**; ***2,2,4-f-4 = +80***; ***2,2,4-f-4' = +16***; ***2,2,4-f-5A = -120***; ***2,2,4-f-5B = +20***). So the "aggregated" spectral changes **Σ *2,2,4-f-i*** for 17 protons are: [9 x (+7)] + [1 x (-256)] + [1 x (-63)] + [1 x (+80)] + [3 x (+16) + [1 x (-120)] + [1 x (+20)] = (+63 -256 -63 +80 +48 -120 +20) = **-228** (≈ **-230 mlrd.**).

These estimations show **that first integral change** (**Σ *2,2,4-e-i***) **is positive by sign, but second** (**Σ *2,2,4-f-i***) **is negative.** We emphasize that **parameter Σ *2,2,4-e-i* is the first example of a such integral parameter with a large positive value** of the previously studied similar integral parameters [2]. When comparing both above calculated parameters (**Σ *2,2,4-e-i*** and **Σ *2,2,4-f-i***) can be seen that the calculations in both cases lead to completely different results (+335 versus -230).

So, the mean parameter **Σ *2,2,4-n-i*** is equal to: **(+335) + (-230) / 2 = +52.5 ≈ +55 mlrd.**

Let's try to find out the reasons for such different values of (**Σ *2,2,4-e-i*** and **Σ *2,2,4-f-i***) parameters. When considering aforesaid octacarbonic fragment $[C^1H^1{}_3\text{-}C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)\text{–}C^3H^3{}_2\text{-}C^4H^4(C^{4'}H^{4'}{}_3)\text{–}C^5H^5{}_2\text{-}]$ you can see that the considered spectral parameters of the first pentacarbonic part ($[C^1H^1{}_3\text{-}C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)\text{–}C^3H^3{}_2\text{-}]$) are approximately equal in both compounds. The main difference we see in terms of different values in a tricarbonic fragment [$\text{-}C^4H^4(C^{4'}H^{4'}{}_3)\text{–}C^5H^5{}_2\text{-}]$ in both cases. The main contribution to the emergence of such a dramatic difference makes, in our opinion, the use of very different values of ***2,2,4-e-4*** on the one hand and ***2,2,5-f-5*** parameters on the other hand (+387 versus +80 **mlrd.**), as well as ***2,2,4-e-5*** and ***2,2,5-f-6*** parameters (+27 versus -70 **mlrd.**). Such differences (but smaller in size) were observed previously for mean "aggregated" spectral changes **Σ *2n-i*** on the one hand and **Σ *Nn-i*** on the other hand when **N** = 3 or 4 [1].

Note also that both calculated parameters (**Σ *2,2,4-e-i*** = **+335 mlrd.**and **Σ *2,2,4-f-i*** = **-230 mlrd.**) for 2,2,4-trimethylalkanes family **2,2,4-n** are much smaller in absolute value than the previously discussed similar parameters for N^1,N^2-dimethylalkanes families N^1,N^2-n (≈ **-500 ÷ 800 mlrd.**, including the smallest one for **2,2-n** family, **Σ *2,2-n-i*** = **-360 mlrd.**), and even the analogous "integral spectral changes" (**-350 ± 30 mlrd.**) that occur when introducing only one methyl group into the molecule of an alkane **n** (i.e. in the **n** → **Nn** (except by the aforementioned case **Σ *2n-i* = -60 mlrd.**). As indicated previously [2], the every of "shortchain" families of dimethylalkanes **2,N²-n** (when $\mathbf{N^1}$ = 2) has the integral changes (**-360 ÷ -565**) much less than the other types of "longchain" families of dimethylalkanes $\mathbf{N^1,N^2}$**-n** (when $\mathbf{N^1}$ = 3 or 4) (**-750 ÷ -820**).

3. 1. 3. The Family of 2,2,3-trimethylalkanes (2,2,3-n).

The carbon atoms in which there are branching (C-2 and C-3) in the family of 2,2,3-trimethylalkanes **2,2,3-n** of the general formula: $C^1H^1{}_3\text{-}C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)\text{–}C^3H^3(C^{3'}H^{3'}{}_3)\text{-}C^4H^4{}_2\text{-}\ \ldots\text{-}C^{n-1}H^{n-1}{}_2\text{-}C^nH^n{}_3$ are not separated by even one methylene groups, ie, are adjacent. Therefore, the most interesting to us is the whole heptacarbonic fragment $[C^1H^1{}_3\text{-}C^2(C^{2'}H^{2'}{}_3)(C^{2''}H^{2''}{}_3)\text{–}C^3H^3(C^{3'}H^{3'}{}_3)\text{-}C^4H^4{}_2\text{–}]$. As in the above case of 2,2,4-trimethylalkanes **2,2,4-n**, as for the previously considered [2] family of 2,3-dimethylalkanes **2,3-n**, for the family of 2,2,3-trimethylalkanes **2,2,3-n** we can expected the mutual influence of two adjacently spaced methyl groups (at C-2 and C-3) on the ***BSP*** values of molecule fragment C-1 –C-4, especially on the proton H-3.

In the sources we use the spectral data of only representatives of the of 2,2,3-trimethylalkanes **2,2,3-n** family: 2,2,3-trimethylbutane **2,2,3-d** are given. This substance like the above 2,2,4-trimethylpentane **2,2,4-e**, we are considering, according to previously accepted definitions [1, 2], as shortchain alkane (because branching at the distal end of the longest chain, i.e., at C-3 is disposed at the β-carbon atom). Moreover, 2,2,3-trimethylbutane **2,2,3-d**, in our opinion, rather is a typical representative of the "branched " than linear alkanes. Due to the fact that in the chosen sources [3, 4] there are no ^{1}H NMR spectral data for other, more long-chain 2,2,3-trimethylalkanes **2,2,3-n** (for example, for the next member of the series - 2,2,3-trimethylpentane **2,2,3-e** – the ^{1}H NMR spectrum data are absent, although the ^{13}C NMR data are presented), when summarized, we shall take into account the existing restriction on the length of the chain.

For 2,2,3-trimethylbutane **2,2,3-d** the protonic spectral data are present in both sources [3,4], and they are consistent with each other. So we'll discuss the details of data [3], as they are presented with greater accuracy, ie to 0.001 ppm (1 **mlrd.**).

In the unsymmetrical molecule of 2,2,3-trimethylbutane **2,2,3-d** the values of base ***2,2,3-d-B-i*** (in **ppm**) and the "standard" differential ***2,2,3-d-i*** (in **mlrd.**) parameters equal to: ***2,2,3-d-B-1*** = ***2,2,3-d-B-2'*** = ***2,2,3-d-B-2''*** = 0.834, ***2,2,3-d-1 = 2,2,3-d-2' = 2,2,3-d-2'' = -46***; ***2,2,3-d-B-3*** = 1.378; ***2,2,3-d-3 = +108***; ***2,2,3-d-B-4*** = ***2,2,3-d-B-3'*** = 0.830; ***2,2,3-d-3' = 2,2,3-d-4 = -50***.

As said above in the studied spectra of 2,2,3-trimethylalkanes **2,2,3-n** family we considered the **"heptacarbonic" fragment** $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4_2\text{-}]$ as the whole **moiety that forming the spectral changes** from the spectrum of the linear alkane. Therefore, the most logical to compare its spectral parameters with the same spectral parameters of **"hexacarbonic" fragment** $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4_2\text{–}]$ as the whole **moiety** in 2,3-dimethylalkanes **2,3-n**.

Then, on the other hand it seems appropriate to compare the "tetracarbonic fragment" $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}]$ in 2,2,3-trimethylbutane **2,2,3-d** with the similar "tetracarbonic fragments" $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}]$ in 2,2-dimethylalkanes **2,2-n**, discussed earlier [2].

Firstly, with the mean parameters of tetracarbonic fragment $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}]$ in longchain 2,2-dimethylalkanes **2,2-n**, discussed previously [2]. Secondly, with the similar parameters of tetracarbonic fragment $[C^1H^1_3\text{-}C^2(C^{2'}H^{2'}_3)(C^{2''}H^{2''}_3)\text{–}]$ in shortchain 2,2-dimethylbutane **2,2-d**, discussed previously [2].

Thirdly, with the such parameters of tricarbonic fragment $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}]$ in shortchain 2,3-dimethylalbutane **2,3-d**, discussed ibid [2].

With regard to fragment $[\text{-}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4_3]$ in 2,2,3-trimethylbutane **2,2,3-d**. The most logical to compare its spectral parameters with the same spectral parameters of the shortchain 2,3-dimethylalbutane **2,3-d**, discussed in [2].

3.1.3.1. Calculations of "additional" differential parameters *2,2,3-d'-1.*

So the first "additional" mean differential parameter designated ***2,2,3-d'-1*** (***2,2,3-d'-1 = 2,2,3-d'-2' = 2,2,3-d'-2''***) we calculated as the difference between the "standard differential parameter ***2,2,3-d-1*** in 2,2,3-trimethylbutane **2,2,3-d** and "standard" mean differential parameters ***2,2-n-1*** in abovementioned longchain 2,2-dimethyalkanes **2,2-n** (***2,2-n-1* = -20mlrd.**, see above**)**. Hence the calculated first "additional" "rounded" differential parameter ***2,2,3-d'-1*** is equal to: ***2,2,3-d-1 - 2,2-n-1*** = [(-46) – (-20] ≈ **-25 mlrd.**

The second "additional" differential parameter designated ***2,2,3-d''-1*** we calculated as the difference between the "standard" differential parameter ***2,2,3-d-1*** in 2,2,3-trimethylbutane **2,2,3-d** and "standard" differential parameter ***2,2-d-1*** in **shortchain** 2,2-dimethylbutane **2,2-d** (***2,2-d-1*= -25mlrd.**[2]**)**. Hence the calculated second "additional" "rounded" differential parameter ***2,2,3-d''-1*** is equal to: (***2,2,3-d-1***) **–** (***2,2-d-1***) = [(-46) – (-25] ≈ **-20 mlrd.**

The third "additional" differential parameter designated ***2,2,3-d'''-1*** we calculated as the difference between the "standard differential parameter ***2,2,3-d-1*** in 2,2,3-trimethylbutane **2,2,3-d** and "standard" mean differential parameters ***2,3-n-1*** in abovementioned longchain 2,3-dimethylalkanes **2,3-n** (***2,3-n-1*= -85mlrd.**[2]**)**. Hence the calculated third "additional" "rounded" differential parameter ***2,2,3-d'''-1*** is equal to: ***2,2,3-d-1 - 2,3-n-1*** = [(-46) – (-85] ≈ **+40 mlrd.**

The fourth "additional" differential parameters designated ***2,2,3-d''''-1*** we again calculated as the difference between the "standard differential parameter ***2,2,3-d-1*** in 2,2,3-trimethylbutane **2,2,3-d** and "standard" differential parameters ***2,3-d-1*** in abovementioned **shortchain** 2,3-dimethylbutane **2,3-d** (***2,3-d-1*= -40 mlrd.**[2]**)**. Hence the calculated fourth "additional" "rounded" differential parameter ***2,2,3-d''''-1*** is equal to: ***2,2,3-d-1 - 2,3-d-1*** = [(-46) – (-40] ≈ **-5 mlrd.**

As shown earlier [2], due to the absence of the carbon chain attached to the atom C-4 in **shortchain** 2,3-dimethylbutane **2,3-d**, this parameter is fundamentally different from the arithmetic mean values of the parameters characteristic of the longchain 2,3-dimethylalkanes **2,3-n**.

Thus all four calculated "additional" differential parameters (***2,2,3-d'-1* = -25 mlrd.** , ***2,2,3-d''-1* = -20 mlrd.** , ***2,2,3-d'''-1* = +40 mlrd.** and ***2,2,3-d''''-1* = -5 mlrd.**) rather differ significantly. In our opinion, is the most suitable are these three "additional" differential parameters ***2,2,3-d'-1***, ***2,2,3-d''-1***,and ***2,2,3-d''''*** because they are calculated for the **shortchain** dimethylbutanes **2,N^2-d** and what is the shortchain 2,2,3-trimethylbutane **2,2,3-d**.

3.1.3.2. Calculations of "additional" differential parameters *2,2,3-d'-3.*

The considered methyne proton H-3 enters into tricarbonic fragment $[-C^{3}H^{3}(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{3}]$ of the 2,2,3-trimethylbutane **2,2,3-d** molecule. Therefore, as mentioned above, it is most advisable to compare parameter ***2,2,3-d-3*** with the same parameter ***2,3-d-3*** in abovementioned shortchain 2,3-dimethylbutane **2,3-d** (***2,2-d-3*** = ***2,2-d-2*** = **+140mlrd.**). Hence, this difference - the calculated "additional" "rounded" differential parameter ***2,2,3-d'-3*** is equal to: ***2,2,3-d-3 - 2,3-d-3*** = [(+108) – (+140] ≈ **-30 mlrd.**

3.1.3.3. Calculations of "additional" differential parameter *2,2,3-d'-4.*

The considered six magnetically equivalent protons (three H-3' protons in $–C^{3'}H^{3'}_{3}$ group and three H-4 protons in $–C^{4}H^{4}_{3}$ group) are present in the tricarbonic fragment $[-C^{3}H^{3}(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{3}]$ of the 2,2,3-trimethylbutane **2,2,3-d** molecule. Therefore, as mentioned above, it is most advisable to compare parameter ***2,2,3-d-3'*** and ***2,2,3-d-4*** with the same parameter ***2,3-d-3'*** and ***2,3-d-4*** in abovementioned shortchain 2,3-dimethylbutane **2,3-d** (***2,3-d-1*** = ***2,3-d-2'*** = ***2,3-d-3'*** = ***2,3-d-4*** = **-40 mlrd.**[2]). Hence, this difference - the calculated "additional" "rounded" differential parameter designated as ***2,2,3-d'-4*** is equal to: ***2,2,3-d-4 - 2,3-d-4*** = (-50) – (-40] ≈ **-10 mlrd.**

3.1.3.4. Calculations of the "aggregated" spectral changes (parameter **Σ** *2,2,3-n-i*) of the 2,2,3-trimethylalkanes family 2,2,3-n.

As shown above, the "aggregated" (integral) spectral changes denoted as **Σ** ***N^1,N^2,N^3-n-i*** (see [2]) in the case of the 2,2,3-trimethylalkanes family **2,2,3-n** referred to as **Σ** ***2,2,3-n-i***.

It is the sum of changes in all the spectral parameters that occurred during the conversion from linear alkanes **n** to the families of **2,2,3-n** trimethylalkanes relatively to the abovementioned **"heptacarbonic"** $[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})-C^{4}H^{4}_{2}-]$ moiety.

Now we calculate this parameter for only members of the **2,2,3-n** trimethylalkanes family – **shortchain** 2,2,3-trimethylbutane **2,2,3-d**. All required values of the "standard" differential spectral parameters ***2,2,3-n-i*** are given in parts 3.1.3.

So the "aggregated" spectral changes **Σ** ***2,2,3-d-i*** for 15 protons are: [9 x (-46)] + [1 x (+108)] + [5 x (-50)] = (-414 +108 -250) = **-556 (≈ -555 mlrd.)**.

These estimations show **that integral change** (**Σ** ***2,2,3-d-i***) **is quite large in size, but negative by sign.** We want to emphasize that discussed parameter **Σ** ***2,2,3-d-i*** is one more example of an **integral parameter of shortchain (rather "branched" than linear) alkanes.** It is this feature we noted in the previous section for the integral parameter **Σ** ***2,2,4-e-I*** (see 3.1.2.6.).

Hence it can be cautious, but very disappointing conclusion. In fact, we do not know what are the real value of the **integral parameters of longchain representatives of the linear 2,2,3-trimethylalkanes family 2,2,3-n.**

3. 1. 4. The spectral parameter's comparison of shortchain representatives of the 2,2,N^3-trimethylalkanes families (2,2,4-n and 2,2,3-n).

Due to lack of required spectral data for longchain 2,2,N^3-trimethylalkanes it appears only valid to compare in this section the shortchain representatives of these families (ie, **2,2,4-e** and **2,2,3-d**). These compounds were assigned to the type of shortchain because in both cases the branching at the distal end of the longest chain (i.e., at C-4 in **2,2,4-e** and C-3 in **2,2,3-d**) is disposed at the β-carbon atom. In cases where the branching is more removed at the distal end of the longest chain, as we saw earlier, there are other rules.

Comparison relates to the mutual “tetracarbonic” fragment $[C^{1}H^{1}_{3}-C^{2}(C^{2'}H^{2'}_{3})(C^{2''}H^{2''}_{3})-]$, the same for both substances, that contains nine protons H^{1}, $H^{2'}$, $H^{2''}$, ie, the tert-butyl fragment C-1 – C-2. It can be considered as a tert-butyl group introduced at a specific location in the molecule of an alkane.

Firstly let’s compare the rounded values of "standard" differential spectral parameters ***2,2,N^{3}-n-1 = 2,2,N^{3}-n-2’ = 2,2,N^{3}-n-2’’*** (which have already been given above) of nine magnetically equivalent methyl protons (see above). The values of the parameters are as follows: ***2,2,3-d-1* = -45 mlrd.**, ***2,2,4-e-1* = +10 mlrd.** Let’s also give the similar parameters of other previously using substances of 2,2-dimethylalkane families: ***2,2-d-1* = -25 mlrd.**, ***2,2-n-1* = -20 mlrd**, ***2,2,5-f-1* = -20 mlrd.**

Secondly let’s present for comparison, the similar rounded parameters of other useful more highly substituted substances of 2,2-dimethylalkane families, spectra of which are also given in the source [3]: ***2,2,3,3-d-B-1*** = 0.863 ppm, rounded ***2,2,3,3-d-1* = -15 mlrd.**, ***2,2,3,4-e-B-1*** = 0.873 ppm, ***2,2,3,4-e-1* = -5 mlrd.**, ***2,2,4,4-e-B-1*** = 0.977 ppm, ***2,2,4,4-e-1* = +95 mlrd.**, ***2,2,4,6,6-g-B-1*** = 0.903 ppm, ***2,2,4,6,6-g-1* = +25 mlrd.**

Let’s divide all of the above 9 types of aforementioned compounds into three groups: a) derivatives of 2,2,3-trimethylalkanes of general formula ***2,2,3,N^{4}-n*** ($N^{3} \neq 4$) and b) derivatives of 2,2,4-trimethylalkanes (which do not contain C-3 methyl group) of general formula ***2,2,4,N^{4},N^{5}-n*** ($N^{3} = 4$); c) the substances of 2,2-dimethylalkane families, which do not contain methyl substituents in any position of "3" or of "4" ($N^{3} \neq 3$ or 4).

The first group will include the following compounds: **2,2,3-d**; **2,2,3,3-d**; **2,2,3,4-e.** The second group will include the following compounds: **2,2,4-e**; **2,2,4,4-e**; **2,2,4,6,6-g.** The third group will include the following compounds: **2,2-d**; other compounds of **2,2-n** family; **2,2,5-f.**

The values of "standard" differential parameters of the first group, denoted as ***2,2,3,N^{4}-n-1,*** have **negative values** (respectively, **-45**, **-15** and **-5 mlrd.**). The values of "standard" differential parameters of the second group, denoted as ***2,2,4,N^{4},N^{5}-n-1,*** opposite have **positive values** (respectively, **+10**, **+95** and **+25 mlrd.**). The values of "standard" differential parameters of the third group, denoted as ***2,2,N^{3}-n-1,*** again have **negative values** (respectively, **-25**, **-20** and **-20 mlrd.**).

On this basis (ie, the sign of "standard" differential spectral parameters values) it seems appropriate to combine the first and a third group of considered substances and contrast them to the substances of second group. That is, the presence of the methyl substituent in alkyl chain position of "4" (at C-4) in the absence of his in alkyl chain position of "3" (at C-3) leads to a **change in the sign** of the parameter in question from **negative to positive**.

Therefore it is possible to make such a cautious conclusion. Introduction of third methyl substituent exactly in position of "4" (at C-4) to form the families of compounds **2,2,4,N^{4},N^{5}-n** leads to a significant increase of the parameter in question (***2,2,4,N^{4},N^{5}-n-1***) in contrast with other similar parameters (***2,2,3,N^{4}-n-1*** or ***2,2,N^{3}-n-1***) of the families of compounds **2,2,3,N^{4}-n** (an introduction of third methyl substituent in position of "3") or **2,2,N^{3}-n** (an introduction of third methyl substituent in position of "5")**.**

Let’s now consider the above results from the standpoint of producing 2,2,N^{3}-trimethylalkanes by introducing of a tert-butyl group into molecule of linear alkane **n** on into molecule of monomethylalkane **Nn**. The substances of 2,2,3-trimethylalkane family **2,2,3-n** are obtained as result of hydrogen atom H-2 (at carbon atom C-2) substitution in molecule of linear alkane **n** by tert-butyl group. The substances of 2,2,N^{3}-trimethylalkane families **2,2,N^{3}-n** (where **N^{3}**= 4,5, etc.) are obtained as result of hydrogen atom H-1 (at carbon atom C-1) substitution in molecule of monomethylalkane **Nn** by tert-butyl group.

In other words, it means that only substitution of hydrogen atom H-1 (in monocarbonic fragment $C^{1}H^{1}_{3}$-) in molecule of 2-monomethylalkane **2n** by tert-butyl group leads to a ***downfield shift of 9 protons signal of tert-butyl group***. In all other cases (substitution of hydrogen atom H-1 in monocarbonic fragment $C^{1}H^{1}_{3}$-) in molecule of N-monomethylalkane **Nn** (where **N**= 4,5, etc.) as well as substitution of hydrogen atom H-2 (at carbon atom C-2 in monocarbonic fragment -$C^{2}H^{2}_{2}$-) in molecule of linear alkane **n** to form 2,2,3-trimethylalkane **2,2,3-n**, occurs ***upfield shift of signal of tert-butyl group.***

The same result (ie, ***upfield shift of signal of tert-butyl group***) is obtained when hydrogen atom H-1 (at carbon atom C-1 in monocarbonic fragment $C^{1}H^{1}_{3}$-) is substituted in molecule of linear alkane **n** by tert-butyl group to form the substances of 2,2-dimethylalkane family **2,2-n**.

In conclusion, let’s consider the “aggregated” (integral) spectral changes of nineprotonic tert-butyl fragment signal denoted as $\Sigma^{t\text{-}Bu}$ $N^1,N^2,N^3\text{-}n\text{-}i$ in the case of the 2,2,3-trimethylalkanes **2,2,3-n** and other above tert-butylcontaining compounds of general formula **2,2,N^3,N^4,N^5-n**. Let’s write positive values of the parameter $\Sigma^{t\text{-}Bu}$ $N^1,N^2,N^3\text{-}n\text{-}i$ in green, and negative – in purple. Moreover, to emphasize the difference between these values, we increase font size with increasing parameter magnitude.

So the “aggregated” spectral changes $\Sigma^{t\text{-}Bu}$ ***2,2-d-i*** for 9 protons of 2,2-dimethylbutane **2,2-d** (***2,2-d-1* = -25 mlrd.**) is equal to: [9 x (-25)] = **-225 mlrd.** The similar mean parameter $\Sigma^{t\text{-}Bu}$ ***2,2-n-i*** for other 2,2-dimethylalkanes **2,2-n** is equal to: [9 x (-20)] = **-180 mlrd.** Respectively, $\Sigma^{t\text{-}Bu}$ ***2,2,3-d-i*** = **-405 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,5-f-i*** = **-180 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,3,3-d-i*** = **-135 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,3,4-e-i*** = **-45 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,4-e-i*** = **+90 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,4,4-e-i*** = **+855 mlrd.** , $\Sigma^{t\text{-}Bu}$ ***2,2,4,6,6-g-i*** = **+225 mlrd.**

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

In the family of 2,3,4-trimethylalkanes **2,3,4-n** of the general formula: $C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{–}\ldots\text{-}C^{n-1}H^{n-1}_2\text{-}C^nH^n_3$ the carbon atoms in which there are branching (C-2, C-3 and C-4), are not separated by even one methylene groups in both cases, ie, are all adjacent.

Therefore, the most interesting to us is the whole octacarbonic fragment **$[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{–}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{–}]$.** For the family of 2,3,4-trimethylalkanes **2,3,4-n**, as in the above cases of 2,2,N^3-trimethylalkanes **2,2,3-n** and **2,2,4-n** families, and for the previously considered [2] families of N^1,N^2-dimethylalkanes **2,3-n** and **3,4-n**, we can expected the mutual influence of all three adjacently spaced methyl groups (at C-2, C-3 and C-4) on the ***BSP*** values of molecule fragment C-1 –C-5 protons.

In the sources we use the spectral data are given of only representatives of the of 2,3,4-trimethylalkanes **2,3,4-n** family: 2,3,4-trimethylpentane **2,3,4-e**. The protonic spectral data for it are present in both sources [3, 4], and they are perfectly coincide with each other. So we’ll discuss the details of data [3], as they are presented with greater accuracy, ie, to 0.001 ppm (1 **mlrd.**), despite the fact that the spectrum in [3] was obtained at a low frequency instrument (90 MHz).

Let’s consider the values of base ***2,3,4-e-B-i*** (in **ppm**) and the "standard" differential ***2,3,4-e-i*** (in **mlrd.**) parameters of 2,3,4-trimethylpentane **2,3,4-e**. In the ^{1}H NMR spectra of the symmetrical 2,3,4-trimethylpentane **2,3,4-e** the protons of methyl groups $C^1H^1_3$ and $C^{2'}H^{2'}_3$ (as well as of methyl groups $C^{4'}H^{4'}_3$ and $C^5H^5_3$) are ***magnetically nonequivalent***. The ***BSP*** values of six highfield methyl protons (labeled as H-1) are ***2,3,4-e-B-1*** = ***2,3,4-e-B-5*** = 0.798 ppm (***2,3,4-e-1* = -82mlrd.,** round to **-80 mlrd.**). The ***BSP*** values of six downfield methyl protons (labeled as H-2’) are ***2,3,4-e-B-2’*** = ***2,3,4-e-B-4’*** = 0.882 ppm (***2,3,4-e-2’* = +2mlrd.,** round to **0 mlrd.**). Calculated "aggregated" parameter designated as ***2,3,4-e-B-1’*** **= (0.798 + 0.882) / 2 = 1680 / 2 = 0.840** ppm (***2,3,4-e-1’* = -40 mlrd.**). The difference between the rounded magnitudes of highfield and lowfield protons ***BSP*** values of the magnetically nonequivalent methyl groups in **2,3,4-e** is equal to: 0 – (-80) = 80 mlrd.

The "standard" and "additional" differential parameters for other protons of **2,3,4-e** are equal to: ***2,3,4-e-B-2*** = ***2,3,4-e-B-4*** = 1.639 ppm (***2,3,4-e-2* = +369 mlrd.,** round to **+370 mlrd.**); ***2,3,4-e-B-3*** = 0.970 ppm (***2,3,4-e-1* = -300 mlrd.**). ***2,3,4-e-B-3’*** = 0.737 ppm (***2,3,4-e-3’* = -143 mlrd.,** round to **-145 mlrd.**).

As said above in the ^{1}H spectra of 2,3,4-trimethylalkanes **2,3,4-n** families including the studied spectra of 2,3,4-trimethylpentane **2,3,4-e** we considered the **“octacarbonic” fragment $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{–}C^5H^5_2\text{-}]$** as the whole **moiety that forming the spectral changes** from the spectrum of the linear alkane. As such, it has no analogues among the previously studied [1, 2] parts of methylalkanes molecules.

We want to emphasize that the said **“octacarbonic”** fragmet in shortchain **2,3,4-e** molecule is not bonded with next carbon atom of the chain (ie, C-6), but bonded with the hydrogen atom H-5. So, **this molecule is shortchain** one. Therefore, the most logical in our opinion is to split this**“octacarbonic”** fragmetonto two virtual parts (see below), and than to compare its spectral parameters with the similar spectral parameters of two previously studied moieties: **“pentacarbonic” fragment $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{–}C^3H^3(C^{3'}H^{3'}_3)\text{–}]$** studied when we considering the spectra of 2,3-dimethylalkanes **2,3-n** families (especially the spectra of shortchain 2,3-dimethylbutane **2,3-d** and midchain 2,3-dimethylpentane **2,3-e**) [2] and tricarbonic fragment $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_3]$ considering above in the section 3.1.2.6. of 2,2,4-trimethylalkanes **2,3,4-n** families.

Another look at the 2,3,4-trimethylpentane **2,3,4-e** molecule involves the splitting it into three virtual parts: two identical above tricarbonic fragments: $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)–]$ and $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_3]$ and one virtual bivalent dicarbonic fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$. The advantage of this approach is the fact that the tricarbonic fragment $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_2\text{-}]$ parameters are considered earlier. Ie, in fact we will only define the spectral parameters of the said bivalent dicarbonic fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$.

Based on the foregoing, we'll calculate two types of "additional" differential parameters ***2,3,4-e'-i***: the "additional" differential parameters ***2,3,4-e'-iA*** for **fragments** $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)–C^3H^3(C^{3'}H^{3'}_3)–]$ and $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_3]$ and second "additional" differential parameters ***2,3,4-e'-iB*** for abovementioned bivalent dicarbonic fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$.

Both of the above approaches are used to calculate of the "aggregated" spectral changes (parameter **Σ** ***2,3,4-e-i***) of the 2,3,4-trimethylalkanes family **2,3,4-n.**

3.2.1. Calculations of "additional" differential "methyl" parameters (2,3,4-e*'-1A*) for virtual fragments $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)–C^3H^3(C^{3'}H^{3'}_3)–]$ and $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_3]$.

3.2.1.1. Calculations of "additional" differential "methyl" parameters 2,3,4-e*'-1* and 2,3,4-e*'-2'* for virtual fragment $[C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)–C^3H^3(C^{3'}H^{3'}_3)–]$.

So the first "additional" differential parameters of 3 methyl protons H-1, designated ***2,3,4-e'-1*** we calculated as the difference between the "standard" differential parameter ***2,3,4-e-1*** in 2,3,4-trimethylpentane **2,3,4-e** and "standard" mean differential parameters ***2,3-n-1*** in abovementioned longchain 2,3-dimethyalkanes **2,3-n** (***2,3-n-1*= -85mlrd.**, see above**).** Hence the calculated first "additional" "rounded" differential parameter ***2,3,4-e'-1*** is equal to: ***2,3,4-e-1* - *2,3-n-1*** = [(-90) – (-85] ≈ **-5 mlrd.**

The first "additional" differential parameters of 3 methyl protons H-2' designated ***2,3,4-e'-2'*** we also calculated as the difference between the "standard differential parameter ***2,3,4-e-2'*** in 2,3,4-trimethylpentane **2,3,4-e** and "standard" mean differential parameters ***2,3-n-2'*** in abovementioned longchain 2,3-dimethyalkanes **2,3-n** (***2,3-n-2'* = -25mlrd.**[2]**).** Hence the calculated first "additional" "rounded" differential parameter ***2,3,4-e'-2'*** is equal to: ***2,3,4-e-2' - 2,3-n-2'1*** = [(0) – (-25] ≈ +25 **mlrd.**

Finally, we calculate the first "additional" "aggregated" differential parameter for arithmetic mean values of six protons H-1 and H-2', using abovementioned "aggregated" parameter (designated as ***2,3,4-e-1'* = -40 mlrd.**) of 2,3,4-trimethylpentane **2,3,4-e** and similar "aggregated" mean parameter (***2,3-n-1'* = -55 mlrd.**) of the longchain substances of 2,3-dimethylalkanes **2,3-n** family (including midchain 2,3-dimethylpentane **2,3-e**)[2]. Hence the calculated first "additional" "rounded" "aggregated" differential parameter designated as ***2,3,4-e'-1'*** is equal to: ***2,3,4-e-1' - 2,3-n-1'*** = [(-40) – (-55] ≈ +15 **mlrd.**

Likewise we calculated the second (calculated relatively the shortchain 2,3-dimethylbutane **2,3-d**) "additional" "aggregated" differential parameters ***2,3,4-e''-1'*** (since both methyl groups $C^1H^1_3$ and $C^{2'}H^{2'}_3$ in 2,3-dimethylbutane **2,3-d** are magnetically equivalent, the "additional" differential parameters are equal to each other [2], ie ***2,3,4-e''-1*** = ***2,3,4-e''-2'*** = ***2,3,4-e''-1'***). So, it is equal to ***2,3,4-e-1* - *2,3-d-1*** = [(-40) – (-40)] = 0 **mlrd.** Thus the second "additional" "aggregated" differential parameters ***2,3,4-e''-1'*** (relatively the shortchain 2,3-dimethylbutane **2,3-d**) quite significantly different (+15 versus 0 **mlrd.**) from first "additional" "aggregated" differential parameters ***2,3,4-e'-1'*** (relatively the longchain 2,3-dimethylalkanes **2,3-n**).

3.2.1.2. Calculations of "additional" “methyne” differential parameters *2,3,4-e’-2* for virtual fragment $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})–]$.

The considered methyne proton H-2 enters into virtual **“pentacarbonic” fragment** $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})\text{-}]$ of the 2,3,4-trimethylpentane **2,3,4-e** molecule. Therefore, as mentioned above, it is most advisable to compare parameter ***2,3,4-e-2*** with the similar mean parameter ***2,3-n-2*** and ***2,3-d-2*** in abovementioned 2,3-dimethylalkanes **2,3-n** (***2,3-n-2* = +280mlrd., *2,3-d-2* = +140mlrd.**) [2]. Hence, this difference - the calculated first "additional" "rounded" differential parameter ***2,3,4-e’-2*** is equal to: ***2,3,4-e-2* - *2,3-n-2*** = = [(+370) – (+280] = **+90 mlrd.** Similarly, the calculated second "additional" "rounded" differential parameter ***2,3,4-e’’-2*** is equal to: ***2,3,4-e-2 - 2,3-d-2***= = [(+370) – (+140] = **+230 mlrd.** Thus the second "additional" differential parameters ***2,3,4-e’’-2*** (relatively the shortchain 2,3-dimethylbutane **2,3-d**) **is very much different** (+230 versus +90 **mlrd.**) from first "additional" differential parameters ***2,3,4-e’-2*** (relatively the longchain 2,3-dimethylalkanes **2,3-n**).

So, as shown earlier [2] and above, due to the absence of the carbon chain attached to the atom C-5 in **shortchain** 2,3,4-trimethylbutane **2,3,4-e**, ***this parameter may be fundamentally different from the arithmetic mean values of the similar parameter characteristic of the longchain*** 2,3,4-trimethylalkanes **2,3,4-n**.

3.2.1.3. Calculations of first "additional" “methyne” differential parameters *2,3,4-e’-3* for virtual fragment $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})–]$.

The considered methyne proton H-3 also enters into virtual **“pentacarbonic” fragment** $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})\text{-}]$ of the 2,3,4-trimethylpentane **2,3,4-e** molecule. Therefore, as mentioned above, it is most advisable to compare parameter ***2,3,4-e-3*** with the similar mean parameter ***2,3-n-3*** in abovementioned longchain 2,3-dimethylalkanes **2,3-n** (***2,3-n-3* = -10mlrd.**) [2]. Hence, this difference - the calculated first "additional" "rounded" differential parameter ***2,3,4-e’-3*** is equal to: ***2,3,4-e-3 - 2,3-n-3***= = [(-300) – (-10] ≈ **-290 mlrd.** Since both methyne protons $C^{2}H^{2}$ and $C^{3}H^{3}$ in shortchain 2,3-dimethylbutane **2,3-d** are magnetically equivalent, the consideration of the second "additional" differential parameter ***2,3,4-e’’-3*** (calculated relatively the shortchain 2,3-dimethylbutane **2,3-d**) is meaningless.

3.2.1.4. Calculations of first "additional" “methyl” differential parameters*2,3,4-e’-3’* for virtual fragment $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})–]$.

The considered three methyl protons H-3’ also enters into virtual **“pentacarbonic” fragment** $[C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})–C^{3}H^{3}(C^{3'}H^{3'}_{3})\text{-}]$ of the 2,3,4-trimethylpentane **2,3,4-e** molecule. Therefore, as mentioned above, it is most advisable to compare parameter ***2,3,4-e-3’*** with the similar mean parameter ***2,3-n-3’*** in abovementioned longchain 2,3-dimethylalkanes **2,3-n** (***2,3-n-3’* = -95mlrd**) [2]. Hence, this difference - the calculated first "additional" "rounded" differential parameter ***2,3,4-e’-3’*** is equal to: ***2,3,4-e-3’ - 2,3-n-3’***= = [(-143) – (-95] ≈ **-50 mlrd.** The calculations of the second "additional" differential parameter ***2,3,4-e’’-3’*** is impractical due to the reasons discussed above in 3.2.1.3.

3.2.2. Calculations of "additional" differential parameters *2,3,4-e’-iB* for virtual fragment $[\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$.

3.2.2.1. Calculations of "additional" differential “methyl” parameter (*2,3,4-e’-5B*) for virtual fragment $[\text{-}C^{4}H^{4}(C^{4'}H^{4'}_{3})–C^{5}H^{5}_{3}]$.

The "additional" differential parameters of 6 methyl protons (three H-4’ and three H-5), designated as *2,3,4-e’-5* we calculated as the difference between the "standard” differential "aggregated" parameter ***2,3,4-e-1’ = (2,3,4-e-4’ + 2,3,4-e-5) / 2*** in 2,3,4-trimethylpentane **2,3,4-e** and "standard" mean differential parameters ***2n-1*** in abovementioned longchain 2-monomethylalkanes **2n** (***2n-1*= -15mlrd.** [1]**)**. Hence the calculated "additional" "rounded" differential parameter ***2,3,4-e'-5*** is equal to: ***2,3,4-e-5 - 2n-1*** = [(-40) – (-15] ≈ -25 mlrd.

3.2.2.2. Calculations of "additional" differential "methyne" parameter (2,3,4-e*'-4B*) for virtual fragment $[-C^4H^4(C^{4'}H^{4'}_3)–C^5H^5_3]$.

The "additional" differential parameters of one methyne proton H-4, designated ***2,3,4-e'-4*** we calculated as the difference between the "standard" differential parameter ***2,3,4-e-4 = 2,3,4-e-2*** in 2,3,4-trimethylpentane **2,3,4-e** and "standard" mean differential parameters ***2n-2*** in abovementioned longchain 2-monomethyalkanes **2n** (***2n-2*** = **= 250 mlrd.**[1])**.** Hence the calculated "additional" "rounded" differential parameter ***2,3,4-e'-4*** is equal to: ***2,3,4-e-4 - 2n-2*** = [(+370) – (+250] ≈ +120 **mlrd.**

3.2.3. Calculations of second "additional" differential parameters 2,3,4*-e''-i* for virtual bivalent fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$.

3.2.3.1. Calculations of the second "additional" "methyne" differential parameters *2,3,4-e''-3.*

The considered methyne proton H-3 enters into abovementioned virtual bivalent dicarbonic fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$ of the 2,3,4-trimethylpentane **2,3,4-e** molecule. Therefore, in our opinion, it is most advisable to compare the parameter ***2,3,4-e-3*** with the similar parameters of methyne protons H-3 in compounds of 3-monomethylalkanes **3n** family, previously studied [1]. The "standard" mean differential parameter ***3n-3*** is equal to **+65 mlrd.** Hence, this difference - the calculated second "additional" "rounded" differential parameter ***2,3,4-e''-3*** is equal to: ***2,3,4-e-3 - 3n-3*** = [(-300) – (+65)] **= -365 mlrd.**

3.2.3.2. Calculations of the second "additional" "methyl" differential parameters *2,3,4-e''-3'.*

The considered three methyl protons H-3' also enters into above virtual bivalent dicarbonic fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$ of the 2,3,4-trimethylpentane **2,3,4-e** molecule. Therefore, in our opinion, it is most advisable to compare parameter ***2,3,4-e-3'*** with the similar parameters of three methyl protons H-3' in compounds of 3-monomethylalkanes **3n** family, previously studied in [1]. The "standard" mean differential parameter ***3n-3'*** is equal to **-35 mlrd.** Hence, this difference - the calculated second "additional" "rounded" differential parameter ***2,3,4-e''-3'*** is equal to: ***2,3,4-e-3' - 3n-3'*** = [(-145) – (-35)] **= -110 mlrd.**

3.2.3. Calculations of third "additional" differential parameters 2,3,4*-e'''-i* for virtual bivalent fragment $[-C^3H^3(C^{3'}H^{3'}_3)–]$.

3.2.3.1. Calculations of the third "additional" "methyne" differential parameters *2,3,4-e'''-3.*

The considered methyne proton H-3 parameter ***2,3,4-e-3*** advisable to compare well with the similar parameters of methyne protons H-3 in compounds of 2,3-dimethylalkanes **2,3-n** family, previously studied [2]. The "standard" mean differential parameter ***2,3-n-3*** is equal to **-10 mlrd.** Hence, this difference - the calculated third "additional" "rounded" differential parameter ***2,3,4-e''-3*** is equal to: ***2,3,4-e-3 - 2,3-n-3*** = [(-300) – (-10)] **= -290 mlrd.**

3.2.3.2. Calculations of the third "additional" “methyl” differential parameters *2,3,4-e’’’-3’.*

The considered three methyl protons H-3’ parameter ***2,3,4-e-3’*** also advisable to compare well with the similar parameters of methyne protons H-3’ in compounds of 2,3-dimethylalkanes **2,3-n** family previously studied [2]. The "standard” mean differential parameter ***2,3-n-3’*** is equal to **-95 mlrd.** Hence, this difference - the calculated third "additional" "rounded" differential parameter ***2,3,4-e’’’-3’*** is equal to: ***2,3,4-e-3’ - 2,3-n-3’*** = [(-145) – (-95)] = **-50 mlrd.**

3.2.4. Calculations of the “aggregated” spectral changes (parameter Σ *2,3,4-e-i*) of the 2,3,4-trimethylalkanes family 2,3,4-n.

As shown above, the “aggregated” (integral) spectral changes denoted as **Σ** ***N^1,N^2,N^3-n-i*** (see [2]) in the case of the 2,3,4-trimethylalkanes family **2,3,4-n** referred to as **Σ** ***2,3,4-n-i***.

It is the sum of changes in all the spectral parameters that occurred during the conversion from linear alkanes **n** to the families of **2,3,4-n** trimethylalkanes relatively to the abovementioned “octacarbonic” **$[C^1H^1{}_3\text{-}C^2H^2(C^{2'}H^{2'}{}_3)\text{–}C^3H^3(C^{3'}H^{3'}{}_3)\text{–}C^4H^4(C^{4'}H^{4'}{}_3)\text{-}C^5H^5{}_2\text{–}]$** moiety.

Now we calculate this parameter for only members of the **2,3,4-n** trimethylalkanes family – **shortchain** 2,3,4-trimethylpentane **2,3,4-e**.

The first method. All required values of the “standard” differential spectral parameters ***2,3,4-e-i*** are given in parts 3.2.

So the “aggregated” spectral changes **Σ** ***2,3,4-e-i*** for 18 protons are: [3 x (-80)] +[3 x (-0)] + [1 x (+370)] + [1 x (-300)] + [3 x (-145)] + [1 x (+370)] + [3 x (-80)] + [3 x (-0)] = (-240 +370 -300 – 435 + 370 - 240) = **-475 mlrd.**

The second method. Let’s calculated the “aggregated” spectral changes **Σ** ***2,3,4-e-i*** for 18 protons as the sum of three terms: two identical parameters of virtual heptaprotonic isopropyl C-1 – C-2 fragment signal denoted as **$\Sigma^{i\text{-}Pr}$** ***2n-i*** = **+160 mlrd.** in the case of the 2-monomethylalkanes **2n** (vide infra) and above virtual tetraprotonic C-3 – C-3’ fragment, which is equal to [1 x (-300)] + [3 x (-145)] = (-300 – 435) = **-735 mlrd.**

So the “aggregated” spectral changes **Σ** ***2,3,4-e-i*** for 18 protons are: [2 x (+160)] + [1 x (-735)] = (+320 – 735) = **-415 mlrd.**

4. General conclusions

1. We have analyzed the protons chemical shifts values in the PMR spectra of five trimethylalkanes compounds of four families of general formula **N^1,N^2,N^3-n** (when **n** is the letter designation of linear alkane, and **N^1, N^2, N^3** are the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**). We calculated the individual (***N^1,N^2,N^2-n-i***) and arithmetic means (***N^1,N^2,N^2-n-i***) “standard” differential parameters (the difference between absorption of studied proton in **N^1,N^2,N^3-n** and its absorption in the **n**) and "additional" differential parameters ***N^1,N^2,N^3-n-i*** (the difference between absorption of studied proton in **N^1,N^2,N^3-n** and its absorption in chosen etalon compound). We calculated the differences between the summaric values of ***N^1,N^2,N^3-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^3-n**, and designated as **Σ** ***N^1,N^2,N^3-n-i***.

2. It is shown that for those types of the trimethylalkanes **2,2,N^3-n** families, in which the carbon atoms **N^2** (**N^2 = 2**) and **N^3** are separated by three or more methylene groups (i.e. in compounds of **2,2,5-n** family, where **$N^3 \geq N^2 + 3$**) , the total parameter **Σ** ***N^1,N^2,N^2-n-i*** is the **arithmetic sum** of the “integral spectral changes” **of the two virtual fragments** : 1) tetracarbonic fragment **Σ** ***5-n-I***, which are calculated for monomethylalkanes **5n** and 2) pentacarbonic fragment **Σ** ***2,2-n-i*** . These summaric parameters are described previously [1, 2].

3. In other three types of the trimethylalkanes **N^1,N^2,N^2-n** families, in which the carbon atoms **N^2** and **N^3** are separated by less than two methylene group (i.e., **$N^2+2 \geq N^3$**), the value of **Σ** ***N^1,N^2,N^3-n-i*** parameter is

determined by the absorption of polycarbonic (heptacarbonic or octacarbonic) fragments in the molecule of the dimethylalkanes **N^1,N^2,N^3-n**, which we **regard as a whole**.

4. We consider the influence of the numerical value of the parameter **N^3** on chemical shifts of nonaprotonic singlet signal of tert-butyl group in trimethylalkanes of families **2,2,N^3-n** and some polymethylalkanes of families **2,2,N^3,N^4-n** and **2,2,N^3,N^4,N^5-n,** etc. It is shown that the decisive role played by the presence or absence of the parameter **N^3 = 4** in trimethylalkane families, or presence of the parameter **N^4 = 4** (in the case of absence of **N^3 = 3** parameter) in polymethylalkane families.

5. Because of lack of considtrtd substances, and especially the paucity of experimental data for long-chain compounds of trimethylalkanes **N^1,N^2,N^3-n** families, we are unable to make valid conclusions about the dependence of studied spectral parameters on the values of **N^1, N^2, N^3,** numbers.

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