The influence of the methyl group positions in monomethylalkane molecules on the chemical shifts values of all carbon atoms in the ^{13}C NMR spectra

Volodymyr Mizyuk, Volodymyr Shibanov
Ukrainian Academy of Printing, Lviv, Ukraine
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Abstract. The carbon chemical shifts values in the CMR spectra of monomethylalkanes of general formula **Nn** (where **n** is the letter designation of linear alkane, and **N** is the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**) of four monomethylalkane families (**2n, 3n, 4n** and **5n**) have analyzed. It is calculated and discussed the individual (***Nn-i***) "standard" differential parameters (the difference between absorption of studied carbon nuclei in all 4 types of **Nn** and its absorption in the lalkane **n**) and the "integral spectral changes" **Σ *N-n-i*** that occur in process **n** → **Nn**.

Keywords: chemical shift, base spectral parameters, "standard" differential parameters, linear alkanes, monomethylalkanes, integral spectral changes, polycarbonic fragments of alkane molecule.

1. Introduction

1.1. General comments

In our previous communications we considered and discussed the peculiar properties of individual "standard" differential parameters (the difference between absorption of studied hydrogen nuclei in mono- [1], di- [2] and trimethylalkanes [3] and absorption of similar nuclei in the unsubstituted linear alkane). In the present study, we consider the change in the ^{13}C NMR spectral properties of the corresponding carbon atom's nuclei during the transition from an unsubstituted linear alkane to monomethylalkane molecule.

We know that substitution of one hydrogen atom at certain carbon atom in the chain of linear alkane molecule by methyl group leads to the different types of monomethylalkane molecules. It is interesting to examine the change in the CMR spectra of such types of monomethylalkanes in comparison with the spectra of the original linear alkanes.

1. 2. Objects of research

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

Linear alkanes as well as their monomethylsubstituted derivatives (monomethylalkanes) depending upon the carbon chain length we conditionally divide into several groups [4]. 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 monomethylalkanes structure denotation

As previously [1], the designation of each of monomethylalkane «**Nn**» molecule consists of two parts: the first numeric of the «**N**» indicates the position of methyl group in the alkyl chain (i.e., the number of carbon atom to which the methyl group in the alkyl chain of **n** attached). Besides, the numeric of the «**N**» specified the family of monomethylalkanes. Then, with a hyphen small letter «**n**» we indicate the name of the alkane. Simultaneously, in numerical terms, this letter «**n**» denotes alkyl chain length (i.e. number of carbon atoms therein). Numbering started with the shortest monocarbonic chain of methane ("a", **n** = 1), although among considered monomethylalkanes there are no derivative of methane "a", ethane («b» , **n** = 2), and propane («c» , **n** = 3). The symbol "d" denotes butane (**n** = 4), «e» - pentane (**n** = 5), «f» - hexane (**n** = 6), «g» - heptane (**n** = 7), «h - octane (**n** = 8), «j» - nonane (**n** = 9), «k» - decane (**n** = 10), «l» - undecane (**n**

= 11) and «m» - dodecane (**n** = 12). For example, 3-methylhexane denoted as «**3f**», and 2-methylheptane denoted as «**2g**». Below example shows the numbering of carbon atoms in all of the families of «**Nn»** monomethylalkanes.

For instance, above compound **3f** of «**3n**» family have described with general structure:

$$C^{1}H^{1}{}_{3}\text{-}C^{2}H^{2}{}_{2}\text{-}C^{3}H^{3}(C^{3'}H^{3'}{}_{3})\text{-}C^{4}H^{4}{}_{2}\text{-}C^{5}H^{5}{}_{2}\ldots\text{-}C^{n-1}H^{n-1}{}_{2}\text{-}C^{n}H^{n}{}_{3}$$

In the above general structure of 3-methylalkanes family **3n** we use the superscript numeric, which indicated the number of every carbon atom in chain, for example, the first and second carbon atoms in the chain denoted respectively as C^1 and C^2. Penultimate and last atoms designated as C^{n-1} and C^n. The second way to identify each carbon chain involves the use of square brackets, for instance: first and penultimate atoms designated, respectively, as: [C-1] and [C-(n-1)].

Each monomethylalkane molecule consist some **several types of one-carbonic fragments**: three types of methyl groups (two “end” and one "mid"), one "methyne-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 (starting site) or in the "long-chain" fragment (completive side) of carbon chain. As previously [1, 2] we use the notions of “monocarbonic fragments” {for instance ($\mathbf{-C^{i}-}$) or [$-C^{i}H^{i}{}_{2}-$]} and "dicarbonic fragment” {for instance "methine fragment" ($-C^{N}-C^{N'}-$) or ([$-C^{N}H^{N}$] – [$C^{N'}H^{N'}{}_{3}$]-)} and polycarbonic fragments (see below).

«Short-chain» fragment comprises less number of carbon atoms from the beginning of the chain to its branching (i.e., to "methyne" carbon atoms C^N, which is part of dicarbonic "methyne fragment " [$-C^{N}-C^{N'}-$]) than the "long-chain" fragment. In symmetrical molecules such concepts are meaningless. Thus, every monomethyl alkane under consideration contain three parts: a) «short-chain» fragment (starting site of the chain) comprises ([C-1] - [C-(N-1)], i.e., (N-1) carbon atoms; b) dicarbonic "methyne fragment" comprises two carbon atoms ([$-C^{N}-C^{N'}$]) and c) "long-chain" fragment (completive side of the chain) comprises {[C-(N+1)] - [C-(n)] carbon atoms [i.e., (n-N) carbon atoms]. In some cases (for example, in the compounds **2l, 3l**, **4m**, see below), we use the so-called "wrong", "reverse numbering" of carbon atoms in the carbon chain. Wherein carbon atom C^n considered the first atom of the chain, the second atom of chain will be [C-(N-1)], etc. So, the last, the terminal carbon atoms in the "reverse numbered" carbon chain is the carbon atom C^1. Herewith the **long-chain fragment becomes the starting site of the chain**; and *vice versa*, the **short-chain fragment becomes the completive side of the chain**.

In alkyl chain in general 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. In the information sources used by us [5, 6] lack the spectral data for such longchain monomethylalkanes that contain the “mid” methyl group at C-6 (ie, **N** = 6) or longer in the chain.

So, the signal of every carbon atom in molecule of monomethylalkane «**Nn**» in the CMR spectra of monomethylalkanes in general designated as «$\boldsymbol{\delta}^{\mathbf{C,Nn}}{}_{i}$». In superscript part we specify: a) the type of the spectrum (C - carbon spectrum), b) the number of substance - **Nn**; c) sometimes in brackets is number of the source of information ([5] or [6]). In the subscript part of notation we specify the number «***i***» of the position of specific «one-carbonic fragment” «***i***» in the alkyl chain. For above example of 3-methylhexane «**3f**», the carbon atom of “mid” methyl group ($-C^{3'}H^{3'}{}_{3}$) which is bonded to an atom C-3, is designated as C-3' . Accordingly, the carbon chemical shift of this methyl group is indicated as «$\boldsymbol{\delta}^{\mathbf{C,3f}}{}_{3'}$».

1. 2. 3. The order of spectral parameters discussion

The discussion of spectral parameters for each of the monomethylalkanes **Nn** families produced by the following scheme. Initially we discuss compounds of **2n** families of monomethyl-substituted alkanes as compounds with branching closest to the begining of the alkyl chain. Then, consequently, the family of **3n**, **4n**, and finally **5n** monomethylalkanes discussed.

2. Experimental part

We used the spectral data (chemical shifts of carbon atoms in the ^{13}C NMR spectra) taken from the literature sources. The choice of literature sources was 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 books [5, 6]. Spectra obtained in other solvent, e.g. CCl4, we do not discuss here. The chemical shift parameters given in [5] (which are usually given up to 0.01 ppm), were obtained using instruments with low-frequency (22.5 or 25 MHz) and high-frequency (75 or 100 MHz). The quality of these spectra we usually estimate approximately the same, so do not specify the frequency of the instrument. The authors of data represented in [5], **give their own attribution** of spectra signals to the absorption of definite types of carbon atom nuclei.

The authors of data represented in [6] (which are usually obtain in instrument with frequency 75 MHz and given up to 0.01 ppm) **do not give** their own attribution of spectra signals; therefore **we do** this by ourselves[1*].

The "literary" values of aliphatic carbon atoms absorption of monomethylalkane **Nn** families, denoted above as "$\delta^{C,Nn}_{i}$", are shown in four Tables located at the beginning of corresponding sections. These values are called by us the **basic spectral parameters** (shortly, ***BSP***, see below) of carbon atoms absorption. If the ***BSP*** value ($\delta^{C,Nn}_{i}$) is used in both sources [5 and 6] , and respective values differ from each other by an amount not more than 0.1 ppm, only figures of [5] are given given in the Table. In some cases when our attribution of spectra signal shown in [6] does not coincides the author's [5] attribution, **we present our attribution indicated in upper line in cell of Table in bold, and author's [5] assignment in parentheses in lower line in this cell.** In these cases the calculation of the differential spectral parameter (see below) we carry out only for our proposed value ($\delta^{C,Nn[6]}_{i}$) of the base spectral parameter.

The calculated values of **differential spectral parameters** (shortly «***DSP***»), referred to as $\Delta\delta^{C,Nn}_{i}$, along with the ***BSP*** values ($\delta^{C,Nn}_{i}$) we use for the convenience in discussing of the results. About ***DSP*** in detail we will say below. The ***DSP values are always given with the "+" or "- " sign***, they should be ***expressed in ppm*** also. When calculating the **mean parameter values** of ***DSP*** and as **all mean *BSP* values** of compounds **Nn**, are **rounded to the nearest number divisible by 0.05 ppm**. We estimate the inaccuracy of measurements as ± 0.10 ppm.

3. Discussion of results

Base spectral parameters. As mentioned above, the chemical shift of the studied carbon atom signals (i.e., its ***BSP***) in the common designation system referred to as "δ^{C}" with using an superscript and subscript symbols. Signal of every carbon atom in molecule of monomethylalkane «**Nn**» in the CMR spectra as stated above in general we designated as «$\delta^{C,Nn}_{i}$». For convenience to simplify the designation due to the failure of an superscript and subscript symbols, in this communication we repeatedly use a new system [1] of designation for each parameter $\delta^{C,Nn}_{i}$ in the CMR spectra of monomethylalkanes. In each case the newly introduced designation is duplicated the old one (i.e., with using of common superscript and subscript symbols such as " $\delta^{C,Nn}_{i}$"). The ***BSP*** values ("$\delta^{C,Nn}_{i}$") in the text are marked with italic black bold font as "***Nn-B-i***". In this type of notation we do not specify the type of the spectrum (ie, C - carbon spectrum). The symbol "***B***" indicates that this parameter is **basic** parameter (***BSP***), and it introduced in order to distinguish the basic parameter from similar abbreviations for the differential spectral parameters (abbreviated ***DSP***, see below). In the above example of the 3-methylhexane **3f** the symbol «***3f-B-3'***» ($\delta^{H,3f}_{3'}$) denotes the magnitude of the chemical shift of the carbon atom [C-3'] of "mid" methyl group – $C^{3'}H^{3'}_{3}$.

For all or most of the compounds of each the families of monomethylalkane **Nn** we calculated the **arithmetic mean value** [1] of the discussed parameter referred to as the ***underlined*** symbol, «***Nn-B-i***».

[1*] *In some cases, we could not reliably attribute some signals in spectra available of [6] to absorption of the specific carbon atoms [C-i]. Therefore, the* ***basis of our research is the signal assignment in the spectra given in [5] and performed by the authors*** *[5]. So,* ***the correctness of the findings made by us*** *in this study largely* ***depends on the correctness of these assignments****.*

Differential spectral parameters. As previously [1-3], the difference between the chemical shift of the every ***i***-th type of carbon atom nuclei (C^i) in discussed now monomethylalkane **Nn** and the same ***i***-th type of carbon atom nuclei in the "standard (etalon) compound”, which we denote as (***etal***), we designate as the **differential spectral parameter** «$\Delta\delta^{C,Nn}_i$» (abbreviated ***DSP***). The corresponding **linear alkanes n with the same number of carbon atoms** taken as **"standard (etalon) compound”** for each family of the linear alkanes **Nn.** So, the ***DSP*** parameters of all carbon atoms of the discussed monomethylalkanes **Nn** are calculated for each of the ***i***- type carbon atom nuclei (C^i) in molecule, as follows: $\Delta\delta^{C,Nn}_i = \delta^{C,Nn}_i - \delta^{C,etal}_i$. And, in our proposed system of notation as: ***D-Nn-i*** = ***Nn-B-i*** - ***etal-B-i***. As previously [1 - 3], the **“standard”** differential spectral parameters we denote a shorter red bold italic symbol: (***DSP*** = ***Nn-i*** instead of «***Nn-D-i***»), wherein no letter «D». The differential parameters ($\Delta\delta^{C,Nn}_i$ or ***D-Nn-I,*** more precisely, ***Nn-i***) as stated above, differ from the base ones ($\delta^{C,Nn}_i$ or ***Nn-B-i***) so that **they have the sign** " + " or " **-** ". If the signal ***Nn-B-i*** ($\delta^{C,Nn}_i$) is located in a stronger field than the standard signal (***etal-B-i***), then the differential parameter ***D-Nn-i*** (more precisely, ***Nn-i***) has the sign " minus" , and *vice versa*. In all four Tables the numerical values of calculated differential parameters ***Nn-i*** painted red.

As previously indicated [4], all "standard (etalon) compoundi” are longchain linear alkanes **n** contain in its molecule the six types of carbon atoms differing in their ***BSP*** magnitude. To calculate the **mean base spectral parameter** ***n-B-i*** for each $\mathbf{C^i}$ (or [C-i]) carbon atom of **long-chain linear alkanes** (carbon chain of which contains at least 10 carbon atoms) we use the previously justified [4] equation: $n\text{-}B\text{-}i = n_\infty\text{-}B\text{-}i_m + \Delta B\text{-}i$. In this equation parameter $n_\infty\text{-}B\text{-}i_m$ means the basic spectral parameters of the “mid” methylene group carbon atoms (i_m) of ***hypothetical infinitely long chain*** (n_∞) alkanes ($n_\infty\text{-}B\text{-}i_m$ = const = **29.75 ppm**), and mean value of parameters **Δ*B-i*** (which are denoted as “increments” [4]), and calculated for each [C-i] carbon atom of alkyl chain. The values of first five “increments” are equal to: **Δ*B-1* = -15.65 ppm** (for [C-1] and [C-n]); **Δ*B-2* = -7.00 ppm** (for [C-2] and [C-n-1]**;** **Δ*B-3* = +2.25 ppm** (for [C-3] and [C-n-2]**;** **Δ*B-4* = -0.30 ppm; Δ*B-5* = -0.05 ppm** [4].

So, the results of calculations of the mean base spectral parameters ***n-B-i*** ($\delta^{C,n}_i$) values of first five carbon atoms of considered in this paper **longchain linear alkanes** (undecane **l** and dodecane **m**), i.e. [C-1], [C-2], [C-3], [C-4] and [C-5], as well as last five atoms [(C-n-4)], [(C-n-3)], [(C-n-2)], [(C-n-1)], [(C-n)], are next.

a) for carbon atoms of the both ending methyl groups - the first type of carbon atoms of the alkyl chain ([C-1] and [C-n], the parameters $\delta^{C,n}_1 = \delta^{C,n}_n$, {or, more precisely, the **mean base spectral parameters *n-B-1* = *n-B-(C-n)*** , which are depicted as $\delta^{C,n}_1$ or ***n-B-1***} are equal to = 29.75 – 15.65 = **14.10 ppm**;

b) for second type of carbon atoms of the alkyl chain (methylene carbon atoms [C-2] and [C-n-1]); the parameter $\delta^{C,n}_2$ {or ***n-B-2* = *n-B-(C-n-1)*** depicted as $\delta^{C,n}_2$ or ***n-B-2***} are equal to = 29.75 – 7.00 = **22.75 ppm**;

c) similarly, ***n-B-3* = *n-B-(C-n-2)* = 32.00 ppm**; ***n-B-4* = *n-B-(C-n-3)* = 29.45 ppm**; ***n-B-5* = *n-B-(C-n-4)* = 29.70 ppm**.

The parameters ***n-B-i*** of the sixth type of carbon atom of the alkyl chain, i.e., of all remaining carbon atoms, starting from [C-6] (i = 6) and ending to (i = [C-n-5]) **are equal** and have a **value** of parameter $n_\infty\text{-}B\text{-}i_m$, i.e., **29.75 ppm.**

Therefore, all **mean differential spectral parameters of methyl groups carbon atoms**, i.e., the end ([C-1] and [C-n]) (and the mid- ([C-N’]) in all families of monomethylalkanes **Nn**, which we refer to as ***Nn-1***), **in longchain methylalkanes Nn** we calculate by the general formula: ***Nn-1* = *Nn-B-1 – 14.1 ppm.*** Similarly, the **differential spectral parameters of carbon atoms C-2(C-n-1) in longchain methylalkanes Nn** we calculate by the general formula: ***Nn-2* = *Nn-B-2 – 22.75 ppm.*** And, correspondingly, ***Nn-3* = *Nn-B-3 – 32.0 ppm***, ***Nn-4* = *Nn-B-4 – 29.45 ppm***, ***Nn-5* = *Nn-B-5 – 29.7 ppm***, ***Nn-6* = *Nn-B-6 – 29.75 ppm.***

If alkyl chain contains less than 10 carbon atoms (ie, in the cases of midchain alkanes), it becomes necessary to consider the **perturbation of magnetic field** of molecule occurring as a result of infinitely long linear alkane chain broke at both ends of the chain. In this cases the medial chain atoms, for instance, such as atoms [C-3], [C-4] and [C-5] in heptane **g** simultaneously be influenced both of the above factors. This effect on the mean base parameter ***n-B-i*** expressed as a sum of corresponding incremets **Δ*B-i*.**, i.e.: $n\text{-}B\text{-}i = n_\infty\text{-}B\text{-}i_m + \Delta B\text{-}i_{start.} + \Delta B\text{-}i_{fin.}$. Thus, in the above example of heptane **g**, the parameter ***g-B-3*** value for [C-3] is equal to: $\mathbf{29.75} + \Delta B\text{-}3_{start.} + \Delta B\text{-}5_{fin.} = 29.75 + 2.25 - 0.05 =$ **31.95 ppm**; the parameter ***g-B-4*** value for

[C-4] is equal to: **29.75** + $\Delta B\text{-}4_{start.}$+ $\Delta B\text{-}4_{fin.}$ = 29.75 - 0.30 – 0.30 = **29.15 ppm**; the parameter ***g-B-5*** value for C-5 is equal to: **29.75** + $\Delta B\text{-}_{start.}$+ $\Delta B\text{-}3_{fin.}$ = 29.75 – 0.05 + 2.25 = **31.95 ppm**.

We hope, that the method of comparison of used relevant parameters (base and differential) allows us to find the regularities (if they exist) of ***BSP*** carbon values taking place with the point of introduction of first methyl group in the molecules of linear alkanes.

3. 1. 1. The family of 2-monomethylalkanes 2n

In the family of 2-methylalkanes **2n** the carbon atom, where chain is branching is [C-2]. Therefore the terminal carbon atom [C-1] and the carbon atom of mid methyl group [C-2'] are **magnetically equivalent** and will be considered together.

Table 1 shows the every carbon atoms nuclei ***BSP*** and ***DSP*** values of seven 2-methylalkanes **2n**. For each compound the upper row of cells shows the values of the individual **base spectral parameters** ($\delta^{C,2n}_{i}$ or ***2n-B-i***), and the bottom row - the rounded to the nearest number divisible by 0.05 ppm individual **differential spectral parameters** ($\Delta\delta^{C,2n}_{i}$ or ***2n-i***).

To calculation of ***DSP*** values of first compounds – 2-methylbutane **2d** - let's calculate for every carbon atoms nuclei of butane chain (as etalon molecule) the value of **mean base spectral parameters *etal-B-i.*** Because of the symmetry of the butane molecule the parameters ***etal-B-1*** = ***d-B-1*** = ***d-B-4*** and ***etal-B-2*** = ***d-B-2*** = ***d-B-3.*** So, the value of parameter ***etal-B-1*** is equal to: 29.75 – 15.65 - 0.30 = **13.80 ppm**; and ***etal-B-2*** is equal to: 29.75 – 7.00 + 2.25 = **25.00 ppm**. In the above equation ***D-Nn-i*** = ***2n-B-i - etal-B-I*** were used two above calculated base spectral parameters ***etal-B-i*** ($\delta^{C,d}_{i}$): ***13.80 ppm*** (i = 1 and 4) and ***25.00 ppm*** (i = 2 and 3).

To calculate the ***DSP*** values of second compound – 2-methylpentane **2e** - we also use next **base spectral parameters *e-B-i*** (which we have calculated the same way)**:** ***14.05 ppm*** (i = 1 and i = 5), ***22.45 ppm*** (i = 2 and i = 4) and ***34.25 ppm*** (i = 3).

To calculate the ***DSP*** values of third compound – 2-methylhexane **2f** - we use next **base spectral parameters *f-B-i*: *14.10 ppm*** (i = 1 and i = 6), ***22.70 ppm*** (i = 2 and i = 5) and ***31.7 ppm*** (i = 3 and i = 4).

To calculate the ***DSP*** values of fourth compound – 2-methylheptane **2g** - we use next **base spectral parameters *g-B-i* : *14.10 ppm*** (i = 1 and 7), ***22.75 ppm*** (i = 2 and 6), ***31.95 ppm*** (i = 3 and 5) and ***29.15 ppm*** (i = 4).

To calculate the ***DSP*** values of fifth compound – 2-methyloctane **2h** - we use next **base spectral parameters *h-B-i*: *14.10 ppm*** (i = 1 and 8), ***22.75 ppm*** (i = 2 and 7), ***32.00 ppm*** (i = 3 and 6) and ***29.40 ppm*** (i = 4 and 5).

To calculate the ***DSP*** values of sixth compound – 2-methynonane **2j** - we use next **base spectral parameters *j-B-i*: *14.10 ppm*** (i = 1 and 8), ***22.75 ppm*** (i = 2 and 7), ***32.00 ppm*** (i = 3 and 6), ***29.45 ppm*** (i = 4 and 5) and ***29.65 ppm*** (i = 5).

Finally, in the case of most longchain 2-methylundecane **2l** for calculations on the above logic has been used next parameters: ***n-B-1* = *n-B-2'* = *n-B-11* = *14.1* ppm; *n-B-2* = *n-B-10* = *22.75* ppm; *n-B-3* = *n-B-9* = *32.0* ppm; *n-B-4* = *n-B-8* = *29.45 ppm; n-B-5* = *n-B-7* = *29.7 ppm*** and ***n-B-6* = *29.75* ppm.**

Here is an example calculation of standard differential parameters. Let's The calculated the parameter ***2f-3*** of the above formula: ***Nn-i* = *D-Nn-i* = *Nn-B-i - etal-B-i***. So, the parameter ***2f-3*** is equal to: 38.96 – 31.7 = 7.26, rounded up to 7.25 ppm.

Table 1

The base spectral parameters (***BSP***) values, i.e. ***2n-B-i*** or $\delta^{C,2n}_{i}$ (chemical shifts of ***i***-type carbon atoms) and their differential spectral parameter (***2n-i*** or $\Delta\delta^{C,2n}_{i}$) of 2-methylalkanes **2n** of the general formula $\mathbf{C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{2}\text{-}\dots\text{-}C^{\omega-1}H^{\omega-1}_{2}\text{-}C^{\omega}H^{\omega}_{3}}$

Num-ber of com-pound	formula	The ***BSP*** values (***2n-B-i*** or $\delta^{C,2n}_{i}$) and ***DSP*** values (***2n-i*** or $\Delta\delta^{C,2n}_{i}$) in ppm of specified number of "***i***-type" carbon atoms										
		[C-1] and [C-2']	[C-2]	[C-3]	[C-4]	[C-5]	[C-6]	[C-7]	[C-8]	[C-9]	[C-10]	[C-11]
2d	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{3}$	22.32	30.02	31.87	11.83	-	-	-	-	-	-	-
		+8.5	+5.0	+6.85	-1.95	-	-	-	-	-	-	-
2e	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{3}$	22.68	27.87	41.56	20.62	14.37	-	-	-	-	-	-
		+8.65	+5.4	+7.3	-1.85	+0.30	-	-	-	-	-	-
2f	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{3}$	22.71	28.15	38.96	29.88	23.14	14.18	-	-	-	-	-
		+8.6	5.45	+7.25	-1.80	+0.45	+0.1	-	-	-	-	-
2g	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{3}$	22.70	28.09	39.17	27.23	32.30	22.84	14.15	-	-	-	-
		+8.6	5.35	+7.2	-1.9	+0.35	+0.1	+0.05	-	-	-	-
2h	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{3}$	22.72	28.15	39.28	27.57	29.80	32.15	22.84	14.15	-	-	-
		+8.6	5.4	+7.3	-1.85	+0.35	+0.15	+0.1	+0.05	-	-	-
2j	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}C^{9}H^{9}_{3}$	22.74	28.14	39.25	27.59	30.10	29.57	32.10	22.74	14.15	-	-
		+8.65	5.4	+7.25	-1.85	+0.45	+0.12	+0.1	+0.05	+0.05	-	-
2l	$C^{1}H^{1}_{3}\text{-}C^{2}H^{2}(C^{2'}H^{2'}_{3})\text{-}C^{3}H^{3}_{2}\text{-}C^{4}H^{4}_{2}\text{-}C^{5}H^{5}_{2}\text{-}C^{6}H^{6}_{2}\text{-}C^{7}H^{7}_{2}\text{-}C^{8}H^{8}_{2}\text{-}C^{9}H^{9}_{2}\text{-}C^{10}H^{10}_{2}\text{-}C^{11}H^{11}_{3}$	22.71	28.08	39.20	27.55	**30.08** (29.79)	**29.86** (30.08)	**29.79** (29.86)	29.49	32.05	22.78	14.13
		+8.6	5.35	+7.2	-1.9	+0.4	+0.1	+0.1	+0.05	+0.05	+0.05	+0.05

Let's now define the mean rounded values of the **differential spectral parameters** (***2n-i*** or $\Delta\delta^{C,2n}_{i}$) of 5 first carbon atoms ([C-1] – [C-5] and [C-2']): ***2n-1, 2n-2, 2n-2', 2n-3, 2n-4, 2n-5***: of discussed 2-methylalkanes **2n.** Seem to us the **most authentic values of the parameters** ***2n-i*** **are values** defined for **most longchain compounds** **2n**: for 2-methylundecane **2l** and (to a lesser degree) for 2-methylnonane **2j**. Hence the **mean rounded values** of the differential spectral parameters ***2n-i*** we define as to: ***2n-1*** = ***2n-2'= +8.6 ppm; 2n-2 = +5.4 ppm; 2n-3 = +7.2 ppm; 2n-4 = -1.9 ppm; 2n-5 = +0.4 ppm.***

It can be assumed that the **perturbation of magnetic field** of molecule, occurring as a result of transition from a linear alkane **n** to 2-monomethylalkane **2n** (ie, when replacement of a hydrogen atom at [C-2] by methyl group occurs), does **not extend substantially more than five carbon atom of carbon chain** ie, at atoms [C-1] – [C-5]. Already for the sixth carbon atom of chain ([C-6]) the basic spectral parameter value ***2n-B-6*** (or $\boldsymbol{\delta}^{C,2n}_{6}$) varies little, compared with the same parameter ***n-B-6*** (or $\boldsymbol{\delta}^{C,2}_{6}$) of linear alkane **n**. This is evidenced that **all** differential spectral parameters ***2l-i,*** (where *i* is 7 to 11) of 2-methylundekane **2l** not exeeded the absolute value of 0.1 ppm (the value adopted by us for the experimental error). Such as the small absolute values were found for the next differential parameters: |***2f-6***| = ***0.1 ppm*** of 2-methylhexane **2f**; |***2g-6***| = ***0.1 ppm;*** |***2g-7***| = ***0.05 ppm*** of 2-methylheptane **2g**; |***2h-7***| = ***0.1 ppm;*** |***2h-8***| = ***0.05 ppm*** of 2-methyloctane **2h** and |***2j-7***| = ***0.1 ppm;*** |***2j-8***| = ***0.05 ppm***, |***2j-9***| = ***0.05 ppm*** of 2-methylnonane **2j**.

Slightly larger in absolute value are calculated with an accuracy of 0.01 ppm for the differential parameters |***2h-6***| = ***0.15 ppm***, |***2j-6***| = ***0.12 ppm*** and |***2l-6***| = ***0.1 ppm*** for **sixth** carbon atoms ([C-6]) in the carbon chains of 2-methyloktane **2h**, 2-methylnonane **2j** and 2 methylundekane **2l,** however, these values do not exceed 0.15 ppm. Perhaps for the sixth carbon atom of chain – [C-6] - the magnitude of the differential parameter of longchain 2-methylalkanes |***2n-6***| (n≥8), albeit slightly, but exceeds the value adopted by us for the experimental error (0.10 ppm). Therefore, as a discussion we can also take values ***2n-6*** ***= +0.1 ppm.***

Thus, it can be assumed that the **perturbation of magnetic field** of molecule as a result of replacement of a hydrogen atom at [C-2] by methyl group in process **n → 2n** does **not extend more than six carbon atom of carbon chain** ie, at atoms [C-1] – [C-6]. In other words, **this effect covers only next three (or four) carbon atoms after a branched chain atom** {in our case there are the [C-3] – [C-5] (or [C-6]) atoms when branched chain atom is [C-2] (N = 2)}.

3. 1. 2. The family of 3-monomethylalkanes 3n

In the family of 3-methylalkanes **3n** the [**C-3] is the such carbon atom, where chain is branching** (ie, N = 3). Therefore the terminal carbon atom [C-1] are **not magnetically equivalent** to carbon atom of mid methyl group [C-3'] and so will not be considered together.

Table 2 shows the every carbon atom's nuclei ***BSP*** and ***DSP*** values of six 3-methylalkanes **3n**. For each compound, as in Table 1, the upper row shows the values of the individual **base spectral parameters** ***3n-B-i***, and the bottom row - the rounded to the nearest number divisible by 0.05 ppm individual **differential spectral parameters** ***3n-i***.

To calculate the ***DSP*** values of first compound –3-methylpentane **3e** as in the case of compound **2e** for every carbon atoms nuclei in the chain we were used all above 5 mean base spectral parameters ***n-B-i***: ***–14.05 ppm*** (i = 1 and 5), ***22.45 ppm*** (i = 2 and 4) and ***34.25 ppm*** (i = 3). As in the case of other 2-methylalkanes **2n** family to calculate the ***DSP*** values of next four compounds, starting from 3-methylhexane **3f** and ending 3-methylundecane **3l** - we also use corresponding **mean base spectral parameters *n-B-i*.**

Table 2

The base spectral parameters (***BSP***) values, i.e. ***3n-B-i*** or $\delta^{C,3n}_i$ (chemical shifts of ***i***-type carbon atoms) and their differential spectral parameter (***3n-i*** or $\Delta\delta^{C,3n}_i$) of 3-methylalkanes **3n** of the general formula $C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3(C^{3'}H^{3'}_3)\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}\ldots\text{-}C^{\omega-1}H^{\omega-1}_2\text{-}C^{\omega}H^{\omega}_3$

Number of compound	formula	The ***BSP*** values (***3n-B-i*** or $\delta^{C,3n}_i$) and ***DSP*** values (***3n-i*** or $\Delta\delta^{C,3n}_i$) in ppm of specified number of "***i***-type" carbon atoms											
		[C-1]	[C-2]	[C-3]	[C-3']	[C-4]	[C-5]	[C-6]	[C-7]	[C-8]	[C-9]	[C-10]	[C-11]
3e	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_3$	11.48	29.27	36.35	18.83	29.27	11.48	-	-	-	-	-	-
		-2.55	+6.8	+2.1	+4.8	+6.8	-2.55	-	-	-	-	-	-
3f	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_3$	11.45	29.68	34.36	19.24	39.20	20.34	14.47	-	-	-	-	-
		-2.65	+7.0	+2.65	+5.15	+7.5	-2.35	+0.35	-	-	-	-	-
3g	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_3$	11.46	29.55	34.58	19.30	36.51	29.65	23.19	14.21	-	-	-	-
		-2.65	+6.8	+2.65	+5.2	+7.35	-2.3	+0.45	+0.1	-	-	-	-
3h	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_3$	11.44	29.68	34.64	19.29	36.83	26.97	32.46	22.88	14.14	-	-	-
		-2.65	+6.95	+2.65	+5.2	+7.45	-2.45	+0.45	+0.15	+0.05	-	-	-
3j	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_2\text{-}C^9H^9_3$	11.45	**29.68** (29.88)	34.60	19.28	36.84	27.26	**29.88** (29.68)	32.15	22.85	14.16	-	-
		-2.65	+6.95	+2.6	+5.2	+7.4	-2.4	+0.45	+0.15	+0.1	+0.05	-	-
3l	$C^1H^1_3\text{-}C^2H^2(C^{2'}H^{2'}_3)\text{-}C^3H^3_2\text{-}C^4H^4_2\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_2\text{-}C^9H^9_2\text{-}C^{10}H^{10}_2\text{-}C^{11}H^{11}_3$	11.45	**29.64** (29.85)	34.57	19.20	36.81	27.27	30.20	**29.85** (29.64)	29.53	32.09	22.82	14.15
		-2.65	+6.9	+2.55	+5.1	+7.35	-2.45	+0.45	+0.15	+0.1	+0.1	+0.05	+0.05

Given extended above assumption that the **perturbation of magnetic field** of molecule, as a result of replacement of a hydrogen atom at [C-2] by methyl group in process **n** → **2n**, does **not extend more than next three (or four) carbon atoms after a branched chain atom.** In our case of 3-methylalkanes **3n** family these three (or four) carbon atoms are the ([C-4] – [C-6]) (or [C-7]), as the branched chain atom [C-N] is [C-3].

Let's define now in the case of 3-methylalkanes **3n** family the **mean rounded values** of the **differential spectral parameters** ***3n-i*** of 7 first carbon atoms ([C-1] – [C-7] and also [C-3']): ***3n-1, 3n-2, 3n-3, 3n-3', 3n-4, 3n-5, 3n-6, 3n-7*** of discussed 3-methylalkanes **3n.** As in the case of 2-methylalkanes **2n** family, it seem to us that the **most authentic values of the parameters *3n-i* are values** defined for **most longchain compounds** **3n**: for 3-methylundecane **3l** and (to a lesser degree) for 3-methylnonane **3j**. Hence the **mean rounded values** of the differential spectral parameters ***3n-i*** we define as to: ***3n-1 = +2.65 ppm; 3n-2 = +6.9 ppm; 3n-3 = +2.6 ppm; 3n-3' = +5.2 ppm; 3n-4 = +7.4 ppm; 3n-5 = -2.45 ppm; 3n-6 = +0.45 ppm; 3n-7 = +0.15 ppm.***

The confirmation of our assumptions about not extending more than next four carbon atoms after a branched chain atom [C-N] (ie, {[C-(N+1)] – [C-(N+5)]}) we see in next. This influence is also small (no more than 0.1 ppm) absolute values of the differential parameters: l***3h-8***l ***= 0.05 ppm*** for [C-8] in 3 methyloctane **3h**, l*3j-8*l = ***0.1 ppm;*** l*3j-9*l = ***0.05 ppm*** for [C-8] and [C-9] in 3-methylnonane **3j**, and l*3l-8*l = l*3l-9*l = ***0.1 ppm;*** l*3l-10*l = l*3l-11*l = ***0.05 ppm*** for [C-8], [C-9], [C-10] and [C-11] in 3-methylundecane **3l**.

3. 1. 3. The family of 4-monomethylalkanes 4n

In the family of 4-methylalkanes **4n** the [**C-4] is the such carbon atom, where chain is branching** (ie, N = 4). Therefore the terminal carbon atom [C-1] is **not magnetically equivalent** to carbon atom of mid methyl group [C-4'] and so will not be considered together.

Table 3 shows the every carbon atom's nuclei ***BSP*** and ***DSP*** values of four 4-methylalkanes **4n**. For each compound, as in Tables 1 and 2, the upper row shows the values of the individual **base spectral parameters** ***4n-B-i***, and the bottom row - the rounded to the nearest number divisible by 0.05 ppm individual **differential spectral parameters** ***4n-i***.

To calculate the ***DSP*** values of all compounds – 4-methylalkanes **4n** (**n = g, h, j**) as in the above cases of compounds **2n** and **3n** for every carbon atoms nuclei in the chain were used corresponding mean base spectral parameters ***n-B-i.***

To calculate the ***DSP*** values of last, most longchain compound – 4-methyldodecane **4m** – we use for 5 first carbon atoms nuclei on starting side and for five last carbon atoms nuclei of completive sides of the carbon chain in the above equation the mean base spectral parameters: ***n-B-1 = n-B-12 = 14.1*** **ppm;** ***n-B-2 = n-B-11 = 22.75*** **ppm;** ***n-B-3 = n-B-10 = 32.0*** **ppm;** ***n-B-4 = n-B-9 = 29.45 ppm; n-B-4' = 14.1*** **ppm** and ***n-B-5 = n-B-8 = 29.7 ppm.*** For two midchain carbon atom nuclei ([C-6] and [C-7]) were used mean midchain parameter: ***n-B-6 = n-B-7 = 29.75*** **ppm**.

Table 3

The base spectral parameters (***BSP***) values, i.e. ***4n-B-i*** or $\delta^{C,4n}_{i}$ (chemical shifts of ***i***-type carbon atoms) and their differential spectral parameter (***4n-i*** or $\Delta\delta^{C,4n}_{i}$) of 4-methylalkanes **4n** of the general formula $\mathbf{C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}\ldots\text{-}C^{\omega\text{-}1}H^{\omega\text{-}1}_2\text{-}C^{\omega}H^{\omega}_3}$

Number of compound	formula	The ***BSP*** values (***4n-B-i*** or $\delta^{C,4n}_{i}$) and ***DSP*** values (***4n-i*** or $\Delta\delta^{C,4n}_{i}$) in ppm of specified number of "***i***-type" carbon atoms												
		[C-1]	**[C-2]**	**[C-3]**	**[C-4]**	**[C-4']**	**[C-5]**	**[C-6]**	**[C-7]**	**[C-8]**	**[C-9]**	**[C-10]**	**[C-11]**	**[C-12]**
4g	$C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_3$	14.46	20.29	39.62	32.41	19.69	39.62	20.29	14.46	-	-	-	-	-
		+0.35	-2.45	+7.65	+3.25	+5.6	+7.65	-2.45	+0.35	-	-	-	-	-
4h	$C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_3$	14.48	20.34	39.67	32.69	19.78	37.01	29.57	23.24	14.22	-	-	-	-
		+0.40	-2.4	+7.65	+3.3	+5.7	+7.6	-2.45	+0.5	+0.1	-	-	-	-
4j	$C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_2\text{-}C^9H^9_3$	14.44	20.28	39.64	**32.67** (32.45)	19.73	37.24	26.92	**32.45** (32.67)	22.86	14.17	-	-	-
		+0.35	-2.45	+7.65	+3.2	+5.65	+7.6	-2.55	+0.45	+0.1	+0.05	-	-	-
4m	$C^1H^1_3\text{-}C^2H^2_2\text{-}C^3H^3_2\text{-}C^4H^4(C^{4'}H^{4'}_3)\text{-}C^5H^5_2\text{-}C^6H^6_2\text{-}C^7H^7_2\text{-}C^8H^8_2\text{-}C^9H^9_2\text{-}C^{10}H^{10}_2\text{-}C^{11}H^{11}_2\text{-}C^{12}H^{12}_3$	14.45	**20.29** (19.74)	39.63	32.68	**19.74** (20.29)	37.29	**27.26** (30.22)	**30.22** (27.26)	29.87	29.54	32.11	22.83	14.14
		+0.35	-2.45	+7.65	+3.25	+5.65	+7.6	-2.5	+0.45	+0.15	+0.1	+0.1	+0.1	+0.05

Given extended above assumption that the **perturbation of magnetic field** of molecule, as a result of replacement of a hydrogen atom at [C-2] by methyl group in process **n** → **2n**, does **not extend more than next four carbon atoms after a branched chain atom,** we see in next. In the case of 4-methylalkanes **4n** family these four carbon atoms are the [C-5] – [C-8] when branched chain atom is [C-4].

Let's define now in the case of 4-methylalkanes **4n** family the **mean rounded values** of the **differential spectral parameters** ***4n-i*** of 8 first carbon atoms ([C-1] – [C-8] and also [C-4']): ***4n-1, 4n-2, 4n-3, 4n-4, 4n-4', 4n-5, 4n-6, 4n-7, 4n-8*** of discussed 4-methylalkanes **4n.** As in the case of 2- and 3-methylalkanes **2n** and **3n** families it seem to us that the **most authentic values of the parameters** ***4n-i*** **are values** defined for **most longchain compounds** **4n**: for 4-methyldodecane **4m** and (to a lesser degree) for 4-methylnonane **4j**. Hence the **mean rounded values** of the differential spectral parameters ***4n-i*** we define as to: ***4n-1* = +0.35 ppm; *4n-2* = -2.45 ppm; *4n-3* = +7.65 ppm; *4n 4* = +3.25 ppm; *4n-4’* = +5.65 ppm; *4n-5* = +7.6 ppm; *4n-6* = -2.5 ppm; *4n-7* = +0.45 ppm; *4n-8* = +0.1 ppm.**

The confirmation of assumptions about not extending more than next four carbon atoms after a branched chain atom [C-N] (ie, [C-(N+1)] – [C-(N+5)]) we see in next. The influence are also small (no more than 0.1 ppm) absolute values of the differential parameters *|4j-9|* = ***0.05 ppm*** for [C-9] in 4-methylnonane **4j**, and *|4m-9|* = *|4m-10|* = *|4m-11|* = ***0.1 ppm;*** *|4m-12|* = ***0.05 ppm*** for [C-9], [C-10], [C-11] and [C-12] in 4-methyldodecane **4m**.

3. 1. 4. The family of 5-monomethylalkanes 5n

In the family of 5-methylalkanes **5n** the [**C-5] is the such carbon atom, where chain is branching** (ie, N = 5). Therefore the both terminal carbon atom [C-1] and [C-9] are **not magnetically equivalent** to carbon atom of mid methyl group [C-5’] and so will not be considered together.

Table 4 shows the every carbon atom’s nuclei ***BSP*** and ***DSP*** values of sole 5-methylalkane **5n** - 5-methylnonane **5j.** In Table 4, the upper row shows the values of the individual **base spectral parameter** ***5j-B-i***, and the bottom row - the rounded to the nearest number divisible by 0.05 ppm individual **differential spectral parameters** ***5j-i***.

To calculate the ***DSP*** values of this compound – symmetrical 5-methylnonane **5j** - we use for every 5 first carbon atom’s nuclei on both sides of the carbon chain all 5 aforecited mean base spectral parameters ***n-B-i*** **($\delta^{C,n}_i$)** in the above equation ***D-Nn-i* = *Nn-B-i* - *etal-B-i***. So, we obtain next results: ***n-B-1* = *n-B-9* = *14.1* ppm; *n-B-2* = *n-B-8* = *22.75* ppm; *n-B-3* = *n-B-7* = *32.0* ppm; *n-B-4* = *n-B-6*= *29.45* ppm; *n-B-5* = *29.65* ppm; *n-B-4’* = *14.1* ppm.**

Table 4

The base spectral parameters (***BSP***) values, i.e. ***5j-B-i*** or $\delta^{C,5j}_i$ (chemical shifts of ***i***-type carbon atoms) and their differential spectral parameter (***5j-i*** or $\Delta\delta^{C,5j}_i$) of 5-methylalkanes **5n** of the general formula **$C^1H^1_3$-$C^2H^2_2$-$C^3H^3_2$-$C^4H^4_2$-$C^5H^5(C^{5'}H^{5'}_3)$-$C^6H^6_2$-$C^7H^7_2$-…-$C^{\omega-1}H^{\omega-1}_2$-$C^{\omega}H^{\omega}_3$**

Number of compound	formula	The ***BSP*** values (***5j-B-i*** or $\delta^{C,5j}_i$) and ***DSP*** values (***5j-i*** or $\Delta\delta^{C,5j}_i$) in ppm of specified number of “***i***-type" carbon atoms									
		C-1	C-2	C-3	C-4	C-5	C-5’	C-6	C-7	C-8	C-9
5j	$C^1H^1_3$-$C^2H^2_2$-$C^3H^3_2$-$C^4H^4_2$-$C^5H^5(C^{4'}H^{4'}_3)$-$C^6H^6_2$-$C^7H^7_2$-$C^8H^8_2$-$C^9H^9_3$	14.21	23.23	29.56	37.00	32.93	19.82	37.00	29.56	23.23	14.21
		+0.1	+0.5	-2.45	+7.55	+3.3	+5.7	+7.55	-2.45	+0.5	+0.1

Given extended above assumption that the **perturbation of magnetic field** of molecule, as a result of replacement of a hydrogen atom at [C-2] by methyl group in process **n** → **2n**, does **not extend more than next four carbon atoms after a branched chain atom**, we see in next. In the case of 5-methylalkanes **5n** family (i.e., for 5-methylnonane **5j** as the as the sole representative of the family) these four carbon atoms are the [C-5] – [C-8] when branched chain atom is [C-4].

Let’s define now in the case of 5-methylalkanes **5n** family the **mean rounded values** (equal to individual parameters ***5j-i***) of the **differential spectral parameter** (***5n-i***) of all 9 carbon atoms ([C-1] – [C-9] and also [C-5’]): ***5n-1, 5n-2, 5n-3, 5n-4, 5n-5, 5n-5’, 5n-6, 5n-7, 5n-8, 5n-9.*** As the sole representative of this family –5-methylnonane **5j** – is **symmetrical** compound, so the **mean rounded values** of the differential spectral parameters ***5n-i*** are equal to: ***5n-1* = *5n-9* = +0.1 ppm; *5n-2* = *5n-8* = +0.5 ppm; *5n-3* = *5n-7* = -2.45 ppm; *5n 4* = *5n-6* = +7.55 ppm; *5n-5* = +3.3 ppm; *5n-5’* = +5.7 ppm.**

3. 1. 5. The families of 8- and 9-monomethylalkanes (reverse numbering)

If we use a reverse numbering of carbon atoms of the alkyl chain (ie, exchange the start and finish of its segments), the above-considered **3l** and **4m** compounds should be considered as derivatives of the 9-methylalkane family («**9l**» and «**9m**»); and compound **2l** – as a derivative of 10-methylalkane family («**10l**»). As an example, we present formula of compound **3l,** which is using reverse numbering "incorrectly named" as "9-methyldodekane» «**9m**».

«incorrect name»:

$$\mathbf{C^1H^1{}_3\text{-}C^2H^2{}_2\text{-}C^3H^3{}_2\text{-}C^4H^4{}_2\text{-}C^5H^5{}_2\text{-}C^6H^6{}_2\text{-}C^7H^7{}_2\text{-}C^8H^8{}_2\text{-}C^9H^9(C^{9'}H^{9'}{}_3)\text{-}C^{10}H^{10}{}_2\text{-}C^{11}H^{11}{}_2\text{-}C^{12}H^{12}{}_3}$$

or in the general form:

$$\mathbf{C^nH^n{}_3\text{-}C^{n\text{-}1}H^{n\text{-}1}{}_2\text{-}C^{n\text{-}2}H^{n\text{-}2}{}_2\text{-}\ldots\text{-}C^{N+2}H^{N+2}{}_2\text{-}C^{N+1}H^{N+1}{}_2\text{-}C^NH^N(C^{N'}H^{N'}{}_3)\text{-}C^{N\text{-}1}H^{N\text{-}1}{}_2\text{-}\ldots\text{-}C^1H^1{}_3}$$

The spectral parameters of compounds **2l**, **3l** and **4m** shown in Tables 1-3. This shows us that, if the "correct numbering" of carbon atoms in the chain acts, so the chemical shifts **only for four atoms** [C-(N+1)] - [C-(N+4)] (which are located after "branch points", ie, diatomic "methyne fragment" {[CN] - [C-N']}), really **differ** from similar nuclei chemical shifts in the respective linear alkanes **n**. Chemical shifts of other atoms of carbon chain finishing segment, ie, (atoms [C-(N+5)] - [Cn]), is almost identical to the chemical shifts of similar atoms in a corresponding linear alkanes **n**.

We can assume that the same situation will occur for the starting segment of the carbon chain (as well as by the aforementioned finishing its segment) in the long chain monomethylalkanes families **6n**, **7n**, and so on; for example, for 9-methylheptadecane C_9H_{19}-CH(CH_3)-C_9H_{19}, the symmetrical homolog of the above "incorrectly named" "9-methyldodecane» «**9m**».

Therefore, it seems logical to do the following generalization. In the ^{13}C spectra of long-chain monomethylalkane families (**6n**, **7n** etc.) ***only*** **chemical shifts of *decacarbonic fragment*** **{[C-(N-4)] – [C-(N-1)] } - [C-(N)] – [C-(N')] - {[C-(N+1)] – [C-(N+4)] }** (other designation: $\mathbf{\text{-}C^{N\text{-}4}H^{N\text{-}4}{}_2\text{-}C^{N\text{-}3}H^{N\text{-}3}{}_2\text{-}C^{N\text{-}2}H^{N\text{-}2}{}_2\text{-}C^{N\text{-}1}H^{N\text{-}1}{}_2\text{-}C^NH^N(C^{N'}H^{N'}{}_3)\text{-}C^{N+1}H^{N+1}{}_2\text{-}C^{N+2}H^{N+2}{}_2\text{-}C^{N+3}H^{N+3}{}_2\text{-}C^{N+4}H^{N+4}{}_2\text{-}}$) **differ** from the chemical shifts of similar atoms in a corresponding linear alkanes **n**. The chemical shifts of other atoms as of starting and of finishing segments of carbon chain, i.e., the carbon atoms in fragments **{[C-1] – [C-(N-5)]}** and **{[C-(N+5)] – [C-n]}**, substantially coincide with similar chemical shifts of atoms in the respective linear alkanes **n**.

3. 2. The comparison of similar mean differential spectral parameters *Nn-i* (or $\Delta\delta^{C,Nn}{}_i$) of four N-monomethylalkanes Nn families (N = 2 – 5).

Previously, we assumed that the **perturbation of magnetic field** of molecule (as a result of replacement of a hydrogen atom at [C-N] by methyl group in process **n** → **Nn**) does **not extend more than next four carbon atoms after a branched chain atom** ([C-N]). For example, in completive side of the carbon chain of molecule **Nn** this influence effects on the carbon atoms [C-(N+1)] – [C-(N+4)]. Further, it's logical to assume that the **perturbation of magnetic field** of molecule influence equally distributed on both sides of molecule alkyl chain, located on both sides of the substituted carbon atom [C-N] (N = 2 – 5), as well as on the mid methyl group $C^NH^N{}_3$, i.e., only for above ***decacarbonic fragment*** **{[C-(N-4)] – [C-(N-1)] } - [C-(N)] – [C-(N')] - {[C-(N+1)] – [C-(N+4)] }.**

It is clear, that in N-methylalkane families **2n**, **3n** and **4n** the starting sides of the carbon chain are short. I.e., the number of carbon atoms in these starting sides of the carbon chain [C-1] – [C-(N-1)] is less than 4. Therefore, it seems appropriate to compare for these families of N-methylalkanes only that four carbon atoms in long enough completive side of the carbon chain [C-(N+1)] – [C-(N+4)] which are disposed after branched chain atom [C-N].

Only in 5-methylalkanes **5n** family the starting side of the carbon chain [C-1] – [C-(N-1)], where N = 5 (i.e., [C-1] – [C-4]) such as the completive side of the carbon chain [C-6] – [C-9] in the aforementioned 5-methylnonane **5j**, contains necessary four carbon atoms. Therefore, we will only **compare** the corresponding **differential spectral parameters** ***Nn-i*** of **carbon atoms in completive side of the carbon chain**, ie, parameters ***Nn-i*** of the carbon atoms [C-(N+1)] – [C-(N+4)] which disposed after branched chain atom [C-N] at enough longchain substances. For reasons discussed above also included here the differential spectral parameters ***5n-j*** of all 10 carbon atoms of 5-methylnonane **5j**.

Let's summarized in Table 5 all differential spectral parameters mean values ***Nn-i*** of carbon atoms [C-(N+1)] – [C-(N+4)], listed above for compounds **2n**, **3n**, **4n** and **5j**. These figures are on the increased size of the font in bold. For completeness, we also give all other **differential spectral parameters** mean values ***Nn-i*** of carbon atoms [C-1)] – [C-(N-1)], listed for these compounds at starting side of the carbon chain. These figures are in normal font in italics.

Table 5

The mean values of differential spectral parameter ***Nn-i*** (N = 2, 3, 4, 5) of N-methylalkanes **2n**, **3n**, **4n** and **5n**.

Number of compounds **Nn** families	The mean ***DSP*** values (***Nn-i*** or $\delta^{C,Nn}_{i}$) in ppm of specified number of "***i***-type" carbon atoms									
	[C-(N-4)]	**[C-(N-3)]**	**[C-(N-2)]**	**[C-(N-1)]**	**[C-N]**	**[C-N']**	**[C-(N+1)]**	**[C-(N+2)]**	**[C-(N+3)]**	**[C-(N+4)]**
2n	-	-	-	*+8.6*	**+5.4**	**+8.6**	**+7.2**	**-1.9**	**+0.4**	**+0.1**
3n			*+2.65*	*+6.9*	**+2.6**	**+5.2**	**+7.4**	**-2.45**	**+0.45**	**+0.15**
4n	-	*+0.35*	*-2.45*	*+7.65*	**+3.25**	**+5.65**	**+7.6**	**-2.5**	**+0.45**	**+0.1**
5n	*+0.1*	*+0.5*	*-2.45*	*+7.55*	**+3.25**	**+5.7**	**+7.55**	**-2.45**	**+0.5**	**+0.1**

Let's comment data of table 5. As shown below, the mean differential spectral parameters **values *Nn-i*** of carbon atoms **[C-(N+1)] – [C-(N+4)]** are very **dependent on the starting sides of the carbon chain length**. The shorter this chain, the more distorted the true results. Therefore, the most distorted results obtained for compounds of **2n** family and **most accurate results - for the compounds of 4n family** (and to a lesser extent for the compounds of **3n** family). On the other hand the most accurate ***Nn-i*** values are obtained for the parameters of most remote carbon atoms [N+4], ie, ***[N+4]n-i*** (and to a lesser extent for the [N+3] atoms - ***[N+3]n-i***) from the branched atom[C-N]. Indeed, the difference between the mean parameter values ***[N+4]n-i*** and ***[N+3]n-I*** (0.1 and 0.45 ppm respectively) **for all four families** of **Nn** compounds does not exceed 0.05 ppm, even less than accepted experimental error (0.10 ppm). Having said that, we can say that all corresponding **mean differential spectral parameters values *Nn-i*** of carbon atoms **[C-(N+1)] – [C-(N+4)]**, as so as of carbon atoms **[C-N]** and **[C-N'] for all four families** of **Nn** are **practically identical**.

Here are the values of general **mean differential spectral parameters values *Nn-i*:** ***Nn-[N] = +3.25 ±0.05 ppm; Nn-[N'] = +5.7 ±0.05 ppm; Nn-[N+1] = +7.55 ±0.05 ppm; Nn-[N+2] = -2.45 ±0.05 ppm; Nn-[N+3] = +0.45 ±0.05 ppm; Nn-[N+4] = +0.1 ±0.05 ppm.***

The mean differential spectral parameters values ***Nn-i*** of carbon atoms **[C-1] – [C-N-1)]** of the carbon chain starting sides also are very dependent on the its length. The most accurate ***Nn-i*** values are obtained for the parameters of most remote from the start of a chain carbon atoms [N-1], ie, parameters of closest to center the branching carbon atom ***[N-1]n-i***. And, especially for the compounds with maximum value number of branched atom[C-N] (N = 4), i.e., for compounds of **4n** family. Indeed, the closest to the above mean values of the parameters ***Nn-i***, as predicted, are the parameter: ***4n-3 = 7.65 ppm*** (above mean value of the symmetrical relatively branching carbon atoms parameter ***Nn-[N+1] = +7.55 ±0.05 ppm***). The remaining carbon atoms of the starting chain side [C-1)] – [C-(N-2)] mean parameters ***Nn-i*** usually are significantly different from the symmetric relative chain branching carbon atoms of the completive side of the carbon chain [C-(N+1)] – [C-n] (including parameters of dicarbonic fragment [C-N] – [C-N']). For example, ***2n-1 = +8.6 ppm*** versus ***Nn-[N+1] = +7.55 ±0.05 ppm; 2n-2 = 5.4 ppm*** versus ***Nn-[N] = +3.25 ±0.05 ppm; 2n-2' = 8.6 ppm*** versus ***Nn-[N'] = +5.7 ±0.05 ppm.***

3. 3. The examples of differential spectral parameters *Nn-i* calculations of some substances of N-monomethylalkanes Nn families (N = 2 – 5)

Here are a few examples of differential spectral parameters ***Nn-i*** calculation performed for some compounds **Nn**, using above mean differential spectral parameters values ***Nn-i*.** In particular, for those compounds, in which we propose to introduce **our values** of base spectral parameters ***Nn-B-i***, taken from [6] (see above Tables). Such substances are: **2l** (parameters ***2l-B-5; 2l-B-6; 2l-B-7***); **3j** (parameters ***3j-B-2; 3j-B-6***); **3l** (parameters ***3l-B-2; 3l-B-7***); **4j** (parameters ***4j-B-4; 4l-B-7***); **4m** (parameters ***4m-B-2;***

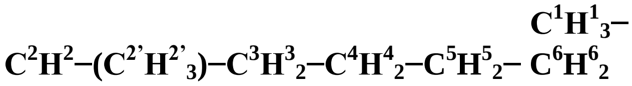
4m-B-4'; 4m-B-6; 4m-B-7). We plan to consider one compound of every monomethylalkane families **2n, 3n, 4n** and **5j**. Among them, we plan to select no less than one midchain substance and no less than one longchain compound. Calculation of the base spectral parameters ***Nn-B-i*** we perform by the procedure described previously [4]. The next scheme used for the convenience of the calculation.

In the top row of every example (in form of Table) there are the basic spectral parameters of the "mid" methylene group carbon atoms (***i**m*) of hypothetical infinitely long chain alkanes (***n***$_\infty$), which are denoted as ***n***$_\infty$***-B-i**m* (δ^C_t).The value of this parameter is the same for all carbon atoms of the studied molecule (***n***$_\infty$***-B-i**m* **= 29.75 ppm**). In the second line we present the abovementioned sum [5] of two increment values [**Δ*B-i*** ($\Delta\delta^C_r$)] (**Δ*B-i**start.* + **Δ*B-i**fin.*) for each "i" carbon atom of molecule, the structural formula of which is shown in the third row. In the fourth row are presented: a) described above 7 **mean differential spectral parameters values *Nn-i*** of next carbon atoms: C-N, C-N' and [C-(N+1)] – [C-(N+5)]; and/or b) 5 **mean differential spectral parameters values *Nn-i*** of next carbon atoms: [C-(N+1)] – [C-(N+5)]. The following (fifth) row shows the ***results of calculation of base spectral parameter Nn-B-i*** according to the formula that used earlier in this article: ***Nn-B-i* = *n***$_\infty$***-B-i**m* + **Δ*B-i**start.* + **Δ*B-i**fin.*+ ***Nn-i.*** In the sixth line we present ***experimental data***, and in the seventh line - the ***difference*** between the calculated and experimental results.

Example 1.

Calculation of all base spectral parameters ***2f-B-i*** of **midchain** representative of the **2-methylalkane** family – 2-methylhexane **2f** and comparing them with experimental data.

Hereinafter the absolute values of Difference: [(***Nn-B-i***)*calc.* - (***Nn-B-i***)*exp.*]**,** which are less than 0.1ppm, painted red.

n$_\infty$***-B-i**m* (δ^C_t), ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75
Δ*B-istart*. + **Δ*B-i**fin.*, ppm	−15.65	−7.05	-15.65	+1.95	+1.95	−7.05	-15.65
 $C^1H^1_3-$ $C^2H^2-(C^{2'}H^{2'}_3)-C^3H^3_2-C^4H^4_2-C^5H^5_2-C^6H^6_2$							
Nn-i and/or **Δ*B-i***, ppm	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1
(***Nn-B-i***)*calc.*, ppm	21.65	25.95	19.80	39.25	29.25	23.15	14.20
(***Nn-B-i***)*exp.*, ppm	**22.71**	**28.15**	**22.71**	**38.96**	**29.88**	**23.14**	**14.18**
Difference: [(***Nn-B-i***)*calc.* - (***Nn-B-i***)*exp.*], ppm	**-1.06**	**-2.2**	**-2.91**	**+0.29**	**-0.63**	**+0.01**	**+0.02**

Example 2.

Calculation of all base spectral parameters ***2l-B-i*** of **longchain** representative of the **2-methylalkane** family – 2-methylundecane **2l** and comparing them with experimental data.

In the sixth row (two lines as above) we present the ***experimental data***, and in the seventh row (also two lines) - the ***difference*** between the **calculated and experimental** results. In those cases (C-5, C-6, C-7), in which our attribution of spectra signal shown in [6] does not coincides the author's [5] attribution, we as above present our attribution in upper line indicated in bold red larger font, and author's [5] assignment in bottom line in ordinary type and in parentheses.

When using our proposed attributing value (top line) of ***2l-B-i*** parameters (where i = 5, 6, 7) the **difference** between the calculated $(2l\text{-}B\text{-}i)_{calc.[6]}$ and experimental $(2l\text{-}B\text{-}i)_{exp.}$ results (top line) **does not exceed the absolute value of 0.1 ppm.**

For this reason, **we believe our attributions are more correct**.

$n_\infty\text{-}B\text{-}i_m$, ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
$\Delta B\text{-}i$, ppm	−15.65	−7.00	-15.65	+2.25	−0.30	−0.05	0	-0.05	-0.30	+2.25	-7.00	-15.65
	$C^1H^1_3$–	C^2H^2–	$(C^{2'}H^{2'}_3)$–	$C^3H^3_2$–	$C^4H^4_2$–	$C^5H^5_2$–	$C^6H^6_2$–	$C^7H^7_2$–	$C^8H^8_2$–	$C^9H^9_2$–	$C^{10}H^{10}_2$–	$C^{11}H^{11}_3$
Nn-i and/or $\Delta B\text{-}i$, ppm	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1	-0.05	-0.30	+2.25	-7.00	-15.65
$(Nn\text{-}B\text{-}i)_{calc.}$, ppm	21.65	26.00	19.80	39.55	27.00	30.15	29.85	29.70	29.45	32.00	22.75	14.10
$(Nn\text{-}B\text{-}i)_{exp.}$, ppm						**30.08**	**29.86**	**29.79**				
	22.71	**28.08**	**22.71**	**39.20**	**27.55**	**(29.79)**	**(30.08)**	**(29.86)**	**29.49**	**32.05**	**22.78**	**14.13**
Difference: $[(Nn\text{-}B\text{-}i)_{calc.} - (Nn\text{-}B\text{-}i)_{exp.}]$						**+0.07**	**-0.01**	**-0.09**				
	-1.06	**-2.08**	**-2.91**	**+0.35**	**-0.55**	**(+0.36)**	**(-0.23)**	**(-0.16)**	**-0.04**	**-0.05**	**-0.03**	**-0.03**

Example 3.

Calculation of all base spectral parameters ***3l-B-i*** of **longchain** representative of the **3-methylalkane** family – 3-methylundecane **3l** and comparing them with experimental data.

As in the previous example N 2, in the rows 6 and 7 were used in each two lines: our attribution of spectra signal shown in [6] in upper line in bold red larger font, and author's [5] assignment in bottom line in ordinary type and in parentheses. When using our proposed attributing value (top line) of $(3l\text{-}B\text{-}i)_{exp.[6]c}$ parameters (where i = 2, 7) the **difference** between the calculated $(3l\text{-}B\text{-}i)_{calc.[6]}$ and experimental $(3l\text{-}B\text{-}i)_{exp.}$ results (top line) **does not exceed the absolute value of 0.1 ppm**.

For this reason**, we believe our attributions are more correct**.

$n_\infty\text{-}B\text{-}i_m$, ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
$\Delta B\text{-}i$, ppm	−15.65	−7.00	+2.25	-15.65	−0.30	−0.05	0	-0.05	-0.30	+2.25	-7.00	-15.65
	$C^1H^1_3$–	C^2H^2–	C^3H^3–	$(C^{3'}H^{3'}_3)$–	$C^4H^4_2$–	$C^5H^5_2$–	$C^6H^6_2$–	$C^7H^7_2$–	$C^8H^8_2$–	$C^9H^9_2$–	$C^{10}H^{10}_2$–	$C^{11}H^{11}_3$
Nn-i and/or $\Delta B\text{-}i$, ppm	-2.45	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1	0	0	0	0
$(Nn\text{-}B\text{-}i)_{calc.}$, ppm	11.65	30.30	33.25	19.8	37.00	27.25	30.2	29.80	29.45	32.00	22.75	14.10
$(Nn\text{-}B\text{-}i)_{exp.}$, ppm		**29.64**						**29.85**				
	11.45	**(29.85)**	**34.57**	**19.20**	**36.81**	**27.27**	**30.20**	**(29.64)**	**29.53**	**32.09**	**22.82**	**14.15**
Difference: $[(Nn\text{-}B\text{-}i)_{calc} - (Nn\text{-}B\text{-}i)_{exp}]$		**+0.66**						**-0.05**				
	+0.20	**(+0.45)**	**-1.32**	**+0.60**	**+0.19**	**-0.02**	**0**	**(+0.16)**	**-0.08**	**-0.09**	**-0.07**	**-0.05**

Example 4.

Calculation of all base spectral parameters ***4m-B-i*** of **longchain** representative of the **4-methylalkane** family – 4-methyldodecane **4m** and comparing them with experimental data.

As in the previous examples N 2 and 3, in each rows 6 and 7 were used two lines: our attribution of spectra signal shown in [6] in upper line in bold red larger font, and author’s [5] assignment in bottom line in ordinary type and in parentheses. When using our proposed attributing value (top line) of **(*4m-B-i*)$_{exp.[6]}$** parameters (where i = 5, 6, 7) the **difference** between the calculated **(*4m-B-i*)$_{calc.}$** and experimental **(*4m-B-i*)$_{exp.}$** results (top line) **does not exceed the absolute value of 0.1 ppm**.

For this reason, **we believe our attributions are more correct**.

n$_\infty$***-B-i***$_m$, ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
Δ*B-i*, ppm	−15.65	−7.00	+2.25	−0.30	−15.65	0	0	0	-0.05	-0.30	+2.25	-7.00	-15.65

$$C^1H^1_3–C^2H^2–C^3H^3_2–C^4H^4–(C^{4'}H^{4'}_3)–C^5H^5_2–C^6H^6_2–C^7H^7_2–C^8H^8_2–C^9H^9_2–C^{10}H^{10}_2–C^{11}H^{11}_2–C^{12}H^{12}_3$$

Nn-i and/or **Δ*B-i***, ppm	+0.45	-2.45	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1	0	0	0	0
(*Nn-B-i*)$_{calc.}$, ppm	14.55	20.30	39.55	32.7	19.8	37.3	27.3	30.2	29.80	29.45	32.00	22.75	14.10
(*Nn-B-i*)$_{exp.}$, ppm		**20.29**			**19.74**		**27.26**	**30.22**					
	14.45	**(19.74)**	**39.63**	**32.68**	**(20.29)**	**37.29**	**(30.22)**	**(27.26)**	**29.87**	**29.54**	**32.11**	**22.83**	**14.14**
Difference: [(***Nn-B-i***)$_{calc}$ - (***Nn-B-i***)$_{exp}$]		**+0.01**			**+0.06**		**+0.04**	**-0.02**					
	+0.10	**(+0.56)**	**-0.08**	**+0.02**	**(-0.49)**	**+0.01**	**(-2.92)**	**(+2.89)**	**-0.07**	**-0.09**	**-0.11**	**-0.08**	**-0.04**

Example 5.

Calculation of all base spectral parameters ***4j-B-i*** of **midchain** (almost longchain) representative of the **4-methylalkane** family – 4-methylnonane **4j** - and comparing them with experimental data.

As in the previous examples N 2 - 4, in each rows 6 and 7 were used two lines: our attribution of spectra signal shown in [6] in upper line in bold red larger font, and author’s [5] assignment in bottom line in ordinary type and in parentheses. When using our proposed attributing value (top line) of **(*4j-B-i*)$_{exp.[6]}$** parameters (where i = 4, 7) the **difference** between the calculated and experimental results (top line) **does not exceed the absolute value of 0.1 ppm**.

For this reason, **we believe our attributions are more correct**.

n$_\infty$***-B-i***$_m$, ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
Δ*B-i*, ppm	−15.65	−7.00	+2.25	−0.30	−15.65	-0.10	-0.30	+2.25	-7.00	-15.65

$$C^1H^1_3–C^2H^2–C^3H^3_2–C^4H^4–(C^{4'}H^{4'}_3)–C^5H^5_2–C^6H^6_2–C^7H^7_2–C^8H^8_2–C^9H^9_3$$

Nn-i and/or **Δ*B-i***, ppm	+0.45	-2.45	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1	0
(*Nn-B-i*)$_{calc.}$, ppm	14.55	20.30	39.55	32.7	19.80	37.2	27.0	32.45	29.85	14.10
(*Nn-B-i*)$_{exp.}$, ppm				**32.67**				**32.45**		

	14.44	**20.28**	**39.64**	**(32.45)**	**19.73**	**37.24**	**26.92)**	**(32.67)**	**29.86**	**14.17**
Difference: [(***Nn-B-i***)$_{calc}$ - (***Nn-B-i***)$_{exp}$**]**	**+0.11**	**+0.02**	**-0.08**	**+0.03** **(+0.25)**	**+0.07**	**-0.04**	**-2.92**	**0.00** **(-0.22)**	**-0.01**	**-0.07**

Example 6.

Calculation of all base spectral parameters ***5j-B-i*** of sole representative of the **5-methylalkane** family – simmetrical **midchain** (almost longchain) 5-methylnonane **5j** and comparing them with experimental data.

Unlike examples 2-5, in example 6 our assignment of spectra signals coincided with the authors [5] assignment.

n$_{\infty}$***-B-i***$_{m}$, ppm	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75
Δ*B-i*, ppm	−15.65	−7.00	+2.25	−0.30	−0.10	−15.65	-0.30	+2.25	-7.00	-15.65

$$C^1H^1_3 - C^2H^2 - C^3H^3_2 - C^4H^4 - C^5H^5 - (C^{5'}H^{5'}) - C^6H^6_2 - C^7H^7_2 - C^8H^8_2 - C^9H^9_3$$

Nn-i and/or **Δ*B-i***, ppm	+0.1	+0.45	-2.45	+7.55	+3.25	+5.7	+7.55	-2.45	+0.45	+0.1
(***Nn-B-i***)$_{calc.}$, ppm	14.2	23.20	29.55	37.0	32.90	19.8	37.0	29.55	23.2	14.2
(***Nn-B-i***)$_{exp.}$, ppm	**14.21**	**23.23**	**29.56**	**37.00**	**32.93**	**19.82**	**37.00**	**29.56**	**23.23**	**14.21**
Difference: [(***Nn-B-i***)$_{calc}$ - (***Nn-B-i***)$_{exp}$**]**	**-0.01**	**-0.03**	**-0.01**	**0.00**	**-0.03**	**-0.02**	**0.00**	**-0.01**	**-0.03**	**-0.01**

Commenting exemplified 1-6 difference **[(*Nn-B-i*)**$_{calc.[6]}$ - **(*Nn-B-i*)**$_{exp}$**]** magnitudes we can see, that these parameters in examples 4-6 (***taking into account the changed us assignments***) **do not exceed the absolute value of 0.1 ppm**. These figures in these examples as above painted in red color.

On the other hand, as expected, carbon atoms of the starting chain side [C-1)] – [C-(N-1)] parameters **[(*Nn-B-i*)**$_{calc.}$ - **(*Nn-B-i*)**$_{exp.}$**]** usually significantly exceed **the absolute value of 0.1 ppm**. The values of these differences usually are negative within the range of from -2.2 {for difference [(***2f-B-2***)$_{calc.}$ - (***2f-B-2***)$_{exp.}$], example N1} to +0.6 ppm {for difference[(***2l-B-3'***)$_{calc.}$ - (***2l-B-3'***)$_{exp.}$], example N3}. In this interval we does not include the value of the parameters [(***2n-B-2'***)$_{calc.}$ - (***2n-B-2'***)$_{exp.}$] [where **n** = 6 (**2f**) and **n** = 11(**2l**)], since by definition parameters [(***2n-B-1***)$_{calc.}$ - (***2n-B-1***)$_{exp.}$] and [(***2n-B-2'***)$_{calc.}$ - (***2n-B-2'***)$_{exp.}$] must be equal. Since these parameters are not equal to each other, it is appropriate to calculate their arithmetic mean. So cited in Example 1 the arithmetic mean of differences [(***2f-B-1***)$_{calc.}$ - (***2f-B-1***)$_{exp.}$] and [(***2f-B-2'***)$_{calc}$ - (***2f-B-2'***)$_{exp.}$] is equal to: (-1.06) + (-2.91) / 2 = ≈ -1.99 ppm, that is less in absolute magnitude than the above value -2.2 ppm. Exactly the same figures were obtained in Example 2 for 2-methylundecane **2l**.

Note that all of our changes in spectral signals assignments lead to a significant reduction of discussed difference parameters **[(*Nn-B-i*)**$_{calc.[6]}$ - **(*Nn-B-i*)**$_{exp.}$**]**. A possible exception is the case of shown in Example N 3, where parameter l[(***3l-B-2***)$_{calc.[6]}$ - (***3l-B-2***)$_{exp.}$]l = 0.66 > l[(***3l-B-2***)$_{calc.[5]}$ - (***3l-B-2***)$_{exp.}$]l = (0.45). In this case, our change of spectral signals assignments leads to a deterioration in the value of this difference (from +0.45 to +0.66 ppm). But interfaced with it parameter [(***3l-B-7***)$_{calc.}$ - (***3l-B-7***)$_{exp.}$] enhances its value (from +0.16 to -0.05 ppm). We believe that this improvement of good predictable difference [(***3l-B-7***)$_{calc.}$ - (***3l-B-7***)$_{exp.}$] is more significant than the degradation of the conjugate parameter [(***3l-B-2***)$_{calc.}$ - (***3l-B-2***)$_{exp.}$], which refers to the unpredictable (as shown above) starting site of alkyl chain.

3. 4. Calculations of the “aggregated” ^{13}C NMR spectral changes (parameter Σ *Nn- i*) of the monomethylalkanes families 2n, 3n, 4n and 5n

As shown earlier for proton spectra of monomethylalkanes **Nn** [1], **the “aggregated” (integral) spectral changes is the sum of changes in all base spectral parameters** that occurred **during the conversion from linear alkanes n to the families of monomethylalkanes Nn** and denoted as **Σ *Nn-i*** (see [2]). It seems appropriate to introduce similar integral parameters for carbon spectra of monomethylalkanes **Nn** also. Their calculation is made on a similar pattern as the sum of **mean differential spectral parameters values *Nn-i*** of next decacarbonic fragment atoms, including: a) {**[C-(N-4)] – [C-(N-1)]**}, b) **C-N, C-N’** and c) {**[C-(N+1)] – [C-(N+4)]**}.

In N-methylalkane families **2n**, **3n** and **4n** the starting side of the carbon chain are short, i.e., the number of carbon atoms in these starting sides of the carbon chain [C-1] – [C-(N-1)] is less than 4 (respectively 1, 2, 3). In these cases, the calculation involves **only available carbon atoms of the starting part** and all four carbon atoms {**[C-(N+1)] – [C-(N+4)]**} of completive sides of the carbon chains (respectively 7, 8, 9 carbon atoms). For instance, in calculation of “aggregated” (integral) spectral parameter **Σ *3n-i*** of 3-methylalkane family **3n** we use the sum of 8 **mean differential spectral parameters values *3n-i*** of next carbon atoms: **[C-(N-2)], [C-(N-1)], C-N, C-N’ and [C-(N+1)] – [C-(N+4)]**, i.e., [C-1], [C-2], [C-3], [C-3’], [C-4], [C-5], [C-6], [C-7].

For the calculation of the integral parameters **Σ *Nn-i*** we assume to use abovementioned general **mean differential spectral parameters values *Nn-i*** for all carbon atoms of completive side of the carbon chains of molecule **Nn** (i.e.,: **C-N, C-N’ and [C-(N+1)] – [C-(N+4)]**) the same for all 4 N-methylalkane families **2n, 3n, 4n** and **5n**. As well as **mean differential spectral parameters values *Nn-i*** for all carbon atoms in starting side of the carbon chain. For every N-methylalkane family (**2n**, **3n** and **4n)** the starting side of the carbon chain as state above is different: for **2n** family it is only one carbon atom - **[C-(N-1)]**; for **3n** family – two carbon atoms: **[C-(N-2)]** and **[C-(N-1)]**; and **4n** family - three carbon atoms: **[C-(N-3)]; [C-(N-2)]** and **[C-(N-1)]**.

However, more accurate values of the integral parameters **Σ *Nn-i*** are obtained, when we use ***individual*** (not general) for each family **mean differential spectral parameters *Nn-i*.** The values of **mean differential spectral parameters *Nn-i*** for each carbon atoms in starting side and four anoms in completive side of the carbon chain are taken from respective above sections: for **2n** family - from section 3.1.1.; for **3n** family - from section 3.1.2.; and for **4n** family - from section 3.1.3. Now let’s calculate integral parameters **Σ *Nn-i*** for all four monomethylalkanes families, using ***individual*** for each family **mean differential spectral parameters *Nn-i***.

So the “aggregated” spectral changes **Σ *2n-i*** for 7 carbon atoms of all 2-methylalkane family **2n** compounds are: [1 x (+8.6)] +[1 x (+5.4)] + [1 x (+8.6)] + [1 x (+7.2)] + [1 x (-1.9)] + [1 x (+0.4)] + [1 x (+0.1)]) = **+28.4 ppm.**

Similarly let’s calculate:

a) the ”aggregated” spectral changes **Σ *3n-i*** for 8 carbon atoms of all 3-methylalkane family **3n** compounds as: = +2.65 +6.9 + 2.6 +5.2 +7.4 -2.45 + 0.45 + 0.15 = **+22.9 ppm.**

b) the ”aggregated” spectral changes **Σ *4n-i*** for 9 carbon atoms of all 4-methylalkane family **4n** compounds as: = +0.35 -2.45 +7.65 + 3.25 +5.65 + +7.6 -2.5 + 0.45 + 0.1 = **+20.1 ppm.**

c) the ”aggregated” spectral changes **Σ *5j-i*** for 10 carbon atoms of 5-methylnonane - only representative of 5-methylalkane family **5n** as: = 0.1 +0.5 -2.45 +7.55 + 3.3 +5.7 +7.55 -2.45 + 0.5 + 0.1 = **+20.4 ppm.**

Comparing all four integral parameters **Σ *Nn-i*** values leads us to the next conclusions.

1) All four integral parameters have a positive value (i.e., **Σ *Nn-i*** > 0 ppm) and these values are approximately equal to 20 ÷ 30 ppm.

2) The values of the integral parameters **Σ *Nn-i*** decreases in the row **Σ *2n-i*** > **Σ *3n-i*** > **Σ *4n-i***, and then practically stabilizes: **Σ *4n-i*** ≈ **Σ *5n-i***.

3) The integral parameter Σ ***2n-i*** approximately one and a half times more than the other three similar parameters (Σ ***3n-i*** , Σ ***4n-i*** and Σ ***5n-i***).

Given the approximate nature of these calculations (the inaccuracy of which we estimate as ± 0.50 ppm.), we can conclude that the **introduction of one methyl substituent in the linear alkane molecule n, leading to the formation of monomethylalkans Nn, accompanied by a significant downfield shift of "aggregated" signas Σ *Nn-i* of remaining and newly formed types carbon atoms**.

The ending

It is of interest to compare the relative integral parameters Σ ***Nn-I*** values, previously [1] calculated for the ^{1}H NMR spectra of four families of monomethylalkanes **Nn** (where **N** = 2 ÷ 5) with similar relative integral parameters Σ ***Nn-i*** values, calculated here for the ^{13}C NMR spectra of these monomethylalkanes **Nn** four families. Note that in both cases, as we move the methyl substituent **$(C^{N'}H^{N'}_{3})$** from the beginning of the carbon chain (**N** = 2) to its mid, the **value of both discussed integral parameters decreases**. Thus, a **negative value** of integral parameters Σ ***Nn-i*** in the protonic spectrum decreases from value (Σ ***Nn-i*** = **-65 ± 50 mlrd.**) for monomethylalkanes **2n** family (when **N = 2**) to value (Σ ***Nn-i*** = **-350 ± 30 mlrd.**) for monomethylalkanes **Nn** families (when **N** = 3, 4, 5). A similar situation occurs with carbonic ^{13}C NMR spectra integral parameters Σ ***Nn-i***. For them, as shown above in Section 3.4., a **positive value** of integral parameters Σ ***Nn-i*** in the carbonic spectrum decreases from value (Σ ***Nn-i*** = **+28.4 ppm**) for monomethylalkanes **2n** family (when **N = 2**) to value (Σ ***Nn-i*** = **+21 ± 1.0 ppm**) for monomethylalkanes **Nn** families (when **N** = 3, 4, 5).

In conclusion, we should say that today we do not understand for what reason the discussed above basic (***Nn-B-i***) and differential (***Nn-i***) ^{13}C NMR spectral parameters (as well as the previously considered in [1] corresponding parameters of the protonic spectra, ie, ^{1}H NMR) for discussed monomethylalkanes **Nn** have such a value. The same applies to the previously studied ^{1}H and ^{13}C NMR spectra of linear alkanes. We hope that further study of the features of these spectra will help to clarify this problem.

4. The general conclusions.

1. We have analyzed the chemical shifts values in the ^{13}C NMR spectra of methylalkanes compounds of general formula **Nn** (when **n** is the letter designation of linear alkane, and **N** is the carbon atom numbers which are attached to the methyl groups in the alkyl chain of **n**). We calculate the individual (***Nn-i***) and arithmetic means (***Nn-i***) "standard" differential parameters (the difference between absorption of studied carbonic anom nuclei in **Nn** and its absorption in the **n**). We calculate the differences between the aggregated values of ***Nn-i*** parameters for **all carbonic anom nuclei in the molecule** of **Nn**. These values we called the "integral spectral changes" that occur in process **n** → **Nn**, and designated as Σ ***Nn-i***.

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

3. The values of the sum parameter (Σ ***Nn-i*** = **+ 28.4 ppm**) of monomethylalkanes **2n** families (when **N = 2**) is **approximately half as much** three types of "longchain" families of dimethylalkanes **Nn** (when **N** = 3, 4, 5) (Σ ***Nn-i*** = **+ 21 ± 1.0 ppm**).

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