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

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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 ($2n$, $3n$, $4n$, $5n$) 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” $\Sigma N-n-i$ that occur in process $n \rightarrow Nn$.

**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:

$$C^1H^1_{-3}C^2H^2_{-2}C^3H^3(\text{C}^3\text{H}^3_{-3})-C^4H^4_{-2}C^5H^5_{-2}...C^n_{n-1}H^n_{n-2}C^nH^n_3$$

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 C₁ and C₂. Penultimate and last atoms designated as Cⁿ⁻¹ and Cⁿ. 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 monocarboic 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 “monocarboic fragments” (for instance [-C^1H]- or [-C^1H^2_{-2}]) and "dicarboic fragment" (for instance "methyne fragment" [-C^N+C^N_{-1}] or [(C^N_{-1}H^N)] - [C^N_{n-1}H^N_{3}]) and polycarboic 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 dicarboic "methyne fragment " [-C^N+C^N_{-1}]) 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) dicarboic "methyne fragment" comprises two carbon atoms ([C^N+C^N_{-1}]) 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^l. 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 «δ^(C,Nn)». 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 {δ} 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\text{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 «δ^{3C,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 beginning 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. CCl$_4$, 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.

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 $\delta^{C}_i$ 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 abbreviated for the differential spectral parameters (abbreviated DSP, see below). In the above example of the 3-methylhexane 3f the symbol $\langle3f-B-3\rangle$ ($\delta^{H,3f}_3$) denotes the magnitude of the chemical shift of the carbon atom [C-3'] of “mid” methyl group – C3®H3®.

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, $\langle Nn-B-i \rangle$.

\footnote{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 in discussed now monomethylalkane \(N_n\) 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 \(\Delta \delta \text{C},N_n\) (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 \(N_n\). So, the DSP parameters of all carbon atoms of the discussed monomethylalkanes \(N_n\) are calculated for each of the \(i\)-type carbon atom nuclei (C) in molecule, as follows: \(\Delta \delta \text{C},N_n \mid _i = \delta \text{C},N_n \mid _i - \delta \text{C},\text{etal} \mid _i\). And, in our proposed system of notation as: \(D-N_n-i = N_n-B_i - \text{etal}-B_i\). As previously [1 - 3], the "standard" differential spectral parameters we denote a shorter red bold italic symbol: \(\text{DSP} = N_n-i\) instead of \(\langle N_n-D-i \rangle\), wherein no letter \(\langle D \rangle\). The differential parameters \((\Delta \delta \text{C},N_n)_{i}\) or \(D-N_n-I\), more precisely, \(N_n-i\) as stated above, differ from the base ones \((\delta \text{C},N_n)_{i}\) or \(N_n-B_i-i\) so that they have the sign " + " or " - ". If the signal \(N_n-B_i-i\) (\(\delta \text{C},N_n\)) is located in a stronger field than the standard signal \((\text{etal}-B_i)\), then the differential parameter \(D-N_n-i\) (more precisely, \(N_n-i\)) has the sign " minus", and vice versa. In all four Tables the numerical values of calculated differential parameters \(N_n-i\) painted red.

As previously indicated [4], all "standard (etalon compound)" are longchain linear alkanes \(n\) contain in its molecule the six types of carbon atoms differing in their \(\text{BSP}\) magnitude. To calculate the mean base spectral parameter \(n-B_i\) for each \(C\) (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: \(n-B_i = n-B_i-m + \Delta B_i\). In this equation parameter \(n-B_i-m\) means the basic spectral parameters of the "mid" methylene group carbon atoms \(\delta \text{C}_i\) of hypothetical infinitely long chain \((n)_i\) alkanes \(n-B_i-m = \text{const} = 29.75 \text{ ppm}\), and mean value of parameters \(\Delta B_i\) (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: \(\Delta B_1 = 15.65 \text{ ppm}\) (for \([C-1]\) and \([C-n]\)); \(\Delta B_2 = 7.00 \text{ ppm}\) (for \([C-2]\) and \([C-n-1]\)); \(\Delta B_3 = 2.25 \text{ ppm}\) (for \([C-3]\) and \([C-n-2]\)); \(\Delta B_4 = -0.30 \text{ ppm}\); \(\Delta B_5 = -0.05 \text{ ppm}\) [4].

So, the results of calculations of the mean base spectral parameters \(n-B_i\) (\(\delta \text{C}_n\)) values of first five carbon atoms of considered in this paper longchain linear alkanes (undecane I 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 \(\delta \text{C}_n = \delta \text{C}_m\) (or, more precisely, the mean base spectral parameters \(n-B_i\) of the ‘mid’ methylene group \(n-B_i = n-B_i-m + \Delta B_i\), which are depicted as \(\delta \text{C}_n\) or \(n-B_i\)) are equal to \(= 29.75 - 15.65 = 14.10 \text{ ppm}\);

b) for second type of carbon atoms of the alkyl chain (methylene carbon atoms \([C-2]\) and \([C-n-1]\)); the parameter \(\delta \text{C}_2\) (or \(n-B_2 = n-B-(C-n-1)\) depicted as \(\delta \text{C}_n\) or \(n-B_2\)) are equal to \(= 29.75 - 7.00 = 22.75 \text{ ppm}\);

c) similarly, \(n-B_3 = n-B-(C-n-2) = 32.00 \text{ ppm}\); \(n-B_4 = n-B-(C-n-3) = 29.45 \text{ ppm}\); \(n-B_5 = n-B-(C-n-4) = 29.70 \text{ ppm}\).

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 \(n-B_{6-m}\), i.e., \(29.75 \text{ ppm}\).

Therefore, all mean differential spectral parameters of methyl groups carbon atoms, i.e., the end \(([C-1]\) and \([C-n]\)) and the mid- \(([C-N^\prime])\) in all families of monomethylalkanes \(N_n\), which we refer to as \(N_n-I\), in longchain methylalkanes \(N_n\) we calculate by the general formula: \(N_n-I = N_n-B_i - 14.11 \text{ ppm}\). Similarly, the differential spectral parameters of carbon atoms \(C-2(C-n-1)\) in longchain methylalkanes \(N_n\) we calculate by the general formula: \(N_n-2 = N_n-B_2 - 22.75 \text{ ppm}\). And, correspondingly, \(N_n-3 = N_n-B_3 - 32.00 \text{ ppm}, N_n-4 = N_n-B_4 - 29.45 \text{ ppm}, N_n-5 = N_n-B_5 - 29.70 \text{ ppm}, N_n-6 = N_n-B_6 - 29.75 \text{ ppm}\).

If alkyl chain contains less than 10 carbon atoms (i.e., 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 increments \(\Delta B_i\), i.e.: \(n-B_i = n-B_{i-m} + \Delta B_{i-start} + \Delta B_{i-fin}\). Thus, in the above example of heptane \(g\), the parameter \(g-B_3\) value for \([C-3]\) is equal to: \(29.75 + \Delta B_{3-start} + \Delta B_{3-fin} = 29.75 + 2.25 - 0.05 = 31.95 \text{ ppm}\); the parameter \(g-B_4\) value for
[C-4] is equal to: \(29.75 + \Delta B-4_{\text{start}} + \Delta B-4_{\text{fin.}} = 29.75 - 0.30 - 0.30 = 29.15 \text{ ppm}\); the parameter \(g-B-5\) value for C-5 is equal to: \(29.75 + \Delta B- \text{start} + \Delta B-3_{\text{fin.}} = 29.75 - 0.05 + 2.25 = 31.95 \text{ ppm}\).

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 \(\text{etal-B-i}\). Because of the symmetry of the butane molecule the parameters \(\text{etal-B-1} = d-B-1 = d-B-4\) and \(\text{etal-B-2} = d-B-2 = d-B-3\). So, the value of parameter \(\text{etal-B-1}\) is equal to: \(29.75 - 15.65 - 0.30 = 13.80 \text{ ppm}\); and \(\text{etal-B-2}\) is equal to: \(29.75 - 7.00 + 2.25 = 25.00 \text{ ppm}\). In the above equation \(D-Nn-i = 2n-B-i - \text{etal-B-1}\)

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.

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

Here is an example calculation of standard differential parameters. Let’s The calculated the parameter \(2f-3\) of the above formula: \(Nn-i = D-Nn-i = Nn-B-i - \text{etal-B-1}\). So, the parameter \(2f-3\) is equal to: 38.96 – 31.7 = 7.26, rounded up to 7.25 ppm.
Table 1

| Num-ber of compound | formula                                                                 | The \(2n-B-i\) values (\(2n-B-i\) or \(\Delta \delta^{C2n}_i\)) of \(2n\) of the general formula \(C^iH^{1-j}C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\) and \(2n\) of the general formula \(C^iH^{1-j}C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\) or \(\Delta \delta^{C2n}_{i+1}\) | \(C-1\) and \(C-2\) | \(C-2\) | \(C-3\) | \(C-4\) | \(C-5\) | \(C-6\) | \(C-7\) | \(C-8\) | \(C-9\) | \(C-10\) | \(C-11\) |
|---------------------|------------------------------------------------------------------------|-------------------------|----------|----------|----------|----------|----------|----------|----------|----------|----------|----------|
| 2d                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.32; 30.02; 31.87; 11.83 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2e                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.68; 27.87; 41.56; 20.62 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2f                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.71; 28.15; 38.96; 29.88 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2g                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.70; 28.09; 39.17; 27.23 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2h                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.72; 28.15; 39.28; 27.57 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2i                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.74; 28.14; 39.25; 27.59 | -        | -        | -        | -        | -        | -        | -        | -        | -        | -        |
| 2l                  | \(C^iH^1\cdot C^iH^2(C^2H^3)\)⋯\(C^iH^{n-2}C^iH^3\)                  | 22.71; 28.08; 39.20; 27.55 | 30.08 (29.79); 29.86 (30.08) | -        | 24.10 | 14.13 | 14.13 | 0.05 | 0.05 | 0.05 |

Let’s now define the mean rounded values of the differential spectral parameters (\(2n-i\) or \(\Delta \delta^{C2n}_i\)) of 5 first carbon atoms ([C-1] – [C-5]) and [C-2]: \(2n-I\), \(2n-2\), \(2n-2\), \(2n-3\), \(2n-4\), \(2n-5\): 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: \(2n-I\) \+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 \(\Delta \delta^{C2n}_6\)) varies little, compared with the same parameter \(n-B-6\) (or \(\delta^{C2n}_6\)) of linear alkane \(n\). This is evidenced that all differential spectral parameters \(2l-i\), \(2l-i\), \(2l-i\) (where \(i\) is 7 to 11) of 2-methylundekane \(2l\) not exceeded 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: \(12j-61\) \+0.1 ppm of 2-methylnexane \(2f\); \(12g-61\) \+0.1 ppm; \(12g-71\) \+0.05 ppm of 2-methylheptane \(2g\); \(12h-71\) \+0.1 ppm; \(12h-81\) \+0.05 ppm of 2-methyloctane \(2h\) and \(12j-71\) \+0.1 ppm; \(12j-81\) \+0.05 ppm, \(12j-91\) \+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 \(12h-61\) \+0.15 ppm, \(12j-61\) \+0.12 ppm and \(12l-61\) \+0.1 ppm for sixth carbon atom ([C-6]) in the carbon chains of 2-methylotkane \(2h\), 2-methylnonane \(2j\) and 2-methylnexene \(2l\), 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 \(12n-61\) \(\geq 8\), 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 \(2n-61\) \+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 \(n \rightarrow 2n\) 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.

The base spectral parameters (BSP) values, i.e. 3n-B-i or δ^{C,3n}_i (chemical shifts of i-type carbon atoms) and their differential spectral parameter (3n-i or Δδ^{C,3n}_i) of 3-methylalkanes 3n of the general formula C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}_{o-1}C^{o}H_{o}^3

<table>
<thead>
<tr>
<th>Number of compound</th>
<th>formula</th>
<th>The BSP values (3n-B-i or δ^{C,3n}_i) and DSP values (3n-i or Δδ^{C,3n}_i) in ppm of specified number of &quot;i&quot;-type carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>3e</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
<tr>
<td>3f</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
<tr>
<td>3g</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
<tr>
<td>3h</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
<tr>
<td>3j</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
<tr>
<td>3l</td>
<td>C^3H_{3+i}C^2H_{2+i}C^1H_{(3^3+i-3)′}C^4H_{4+i}C^5H_{5+i}C^6H_{6+i}C^7H_{7+i}…C^{o-1}H^{o-1}<em>{o-1}C^{o}H</em>{o}^3</td>
<td></td>
</tr>
</tbody>
</table>

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 (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’ = +6.9 ppm; 3n-4 = +7.4 ppm; 3n-5 = +10.45 ppm; 3n-6 = +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: 13h-81 = 0.05 ppm for [C-8] in 3
methylalkanes 3h, $\text{13j-8l} = 0.1 \text{ ppm}$; $\text{13j-9l} = 0.05 \text{ ppm}$ for [C-8] and [C-9] in 3-methylnonane 3j, and $\text{13l-8l} = \text{13l-9l} = 0.1 \text{ ppm}$; $\text{13l-10l} = \text{13l-11l} = 0.05 \text{ ppm}$ 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 $\text{BSP}$ and $\text{DSP}$ 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 $4n-B$, and the bottom row - the rounded to the nearest number divisible by 0.05 ppm individual differential spectral parameters $4n-i$.

To calculate the $\text{DSP}$ 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 $n-B$.

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

The base spectral parameters (BSP values), i.e. $4n-B$ or $\delta^C_{4n}$ (chemical shifts of $i$-type carbon atoms) and their differential spectral parameter ($4n-i$ or $\Delta\delta^C_{4n}$) of 4-methylalkanes 4n of the general formula $\text{C}_8\text{H}_{13}-\text{C}_6\text{H}_{2}-\text{C}_4\text{H}_{5}-\text{C}^4\text{H}^5-\text{C}^3\text{H}^6-\text{C}^2\text{H}^7-\text{C}^1\text{H}^8-\text{C}^0\text{H}^9$ and $\Delta\delta^C_{4n}$ in ppm of specified number of "$i$-type carbon atoms"

<table>
<thead>
<tr>
<th>Number of compound</th>
<th>formula</th>
<th>The $\text{BSP}$ values ($4n-B$-i or $\delta^C_{4n}$) and $\text{DSP}$ values ($4n-i$ or $\Delta\delta^C_{4n}$) in ppm of specified number of &quot;$i$-type carbon atoms&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>4g</td>
<td>$\text{C}<em>8\text{H}</em>{13}-\text{C}<em>6\text{H}</em>{2}-\text{C}<em>4\text{H}</em>{5}-\text{C}^4\text{H}^5-\text{C}^3\text{H}^6-\text{C}^2\text{H}^7-\text{C}^1\text{H}^8-\text{C}^0\text{H}^9$</td>
<td>$14.46 \quad 20.29 \quad 39.62 \quad 32.41 \quad 19.69 \quad 39.62 \quad 20.29 \quad 14.46 \quad$</td>
</tr>
<tr>
<td>4h</td>
<td>$\text{C}<em>8\text{H}</em>{13}-\text{C}<em>6\text{H}</em>{2}-\text{C}<em>4\text{H}</em>{5}-\text{C}^4\text{H}^5-\text{C}^3\text{H}^6-\text{C}^2\text{H}^7-\text{C}^1\text{H}^8-\text{C}^0\text{H}^9$</td>
<td>$14.48 \quad 20.34 \quad 39.67 \quad 32.69 \quad 19.78 \quad 37.01 \quad 29.57 \quad 23.24 \quad 14.22 \quad$</td>
</tr>
<tr>
<td>4j</td>
<td>$\text{C}<em>8\text{H}</em>{13}-\text{C}<em>6\text{H}</em>{2}-\text{C}<em>4\text{H}</em>{5}-\text{C}^4\text{H}^5-\text{C}^3\text{H}^6-\text{C}^2\text{H}^7-\text{C}^1\text{H}^8-\text{C}^0\text{H}^9$</td>
<td>$14.44 \quad 20.28 \quad 39.64 \quad 32.67 \quad (32.45) \quad 19.73 \quad 37.24 \quad 26.92 \quad (32.67) \quad 22.86 \quad 14.17 \quad$</td>
</tr>
<tr>
<td>4m</td>
<td>$\text{C}<em>8\text{H}</em>{13}-\text{C}<em>6\text{H}</em>{2}-\text{C}<em>4\text{H}</em>{5}-\text{C}^4\text{H}^5-\text{C}^3\text{H}^6-\text{C}^2\text{H}^7-\text{C}^1\text{H}^8-\text{C}^0\text{H}^9$</td>
<td>$14.45 \quad 20.29 \quad (19.74) \quad 39.63 \quad 32.68 \quad 19.74 \quad 37.29 \quad 27.26 \quad (30.22) \quad 30.22 \quad (27.26) \quad 29.87 \quad 29.54 \quad 32.11 \quad 22.83 \quad 14.14 \quad$</td>
</tr>
</tbody>
</table>

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 $n \to 2n$, 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-methylundecane 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 $14j-9i = 0.05$ ppm for [C-9] in 4-methylene nonane $4j$, and $14m-9i = 14m-10i = 14m-11i = 0.1$ ppm; $14m-12i = 0.05$ ppm for [C-9], [C-10], [C-11] and [C-12] in 4-methyl dodecane $4m$.

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 $n-B-i$ ($\delta_i^{5n}$) 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.

The base spectral parameters ($BSP$) values, i.e. 5j-B-i or $\delta_i^{5j}$, (chemical shifts of i-type carbon atoms) and their differential spectral parameter (5j-i or $\Delta_i^{5j}$) of 5-methylalkanes 5n of the general formula $C^i$H$_3$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$($C^i$H$_3$)-C$^i$H$_6$-C$^i$H$_7$-C$^i$H$_7$=...-$C^{0-1}$H$^{0-1}$-2-$C^{0-1}$H$^{0-1}$-3

<table>
<thead>
<tr>
<th>Number of compound</th>
<th>formula</th>
<th>$BSP$ values (5j-B-i or $\delta_i^{5j}$) and $DSP$ values (5j-i or $\Delta_i^{5j}$) in ppm of specified number of “i-type” carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C-1</td>
<td>C-2</td>
</tr>
<tr>
<td>5j</td>
<td>$C^i$H$_3$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$-C$^i$H$_2$($C^i$H$_3$)-C$^i$H$_6$-C$^i$H$_7$-C$^i$H$_7$-C$^i$H$_4$</td>
<td>14.21</td>
</tr>
<tr>
<td></td>
<td>$\delta_1^{5j}$</td>
<td>$\delta_2^{5j}$</td>
</tr>
</tbody>
</table>

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 $n \rightarrow 2n$, 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-methyl dodecane" «9m».
incorrect name:

\[
C^1H^1_2_3-C^2H^2_2_2-C^3H^3_2_2-C^4H^4_2_2-C^5H^5_2_2-C^6H^6_2_2-C^7H^7_2_2-C^8H^8_2_2-C^9H^9_2_2-\]
\[
(C^9H^9_3)-C^{10}H^{10}_2_2-C^{11}H^{11}_2_2-
\]
\[
C^{12}H^{12}_3
\]

or in the general form:

\[
C^aH^a_2_3-C^bH^b_2_2-C^{b+1}H^{b+1}_2_2-\ldots-C^{n+2}H^{n+2}_2_2-C^{N+1}H^{N+1}_2_2-C^{N}H^{N}_2_2-\ldots-C^{1}H^{1}_2_2
\]

The spectral parameters of compounds 2I, 3I 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 for atoms [C-(N+1)] - [C-(N+4)] (which are located after "branch points", i.e., 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, i.e., (atoms [C-(N+5)] - [Cn]), is almost identical to the chemical shifts of similar atoms in a corresponding linear alkane 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\(_9\)H\(_{19}\)-CH\(_2\)(CH\(_3\))CH\(_3\), the symmetrical homolog of the above "incorrectly named" "9-methylododecane" 9m.

Therefore, it seems logical to do the following generalization. In the 13C spectra of long-chain monomethylalkane families (6n, 7n etc.) only chemical shifts of decarbonic fragment [(C-(N-1)] - [C-(N-4)] - [C-(N)] - [C-(N')]) - [(C-(N+1)] - [C-(N+4)] \] (other designation: \(C^{N+1}H^{N+1}_2_2-C^{N+2}H^{N+2}_2_2-C^{N+3}H^{N+3}_2_2-C^{N+4}H^{N+4}_2_2\)) differ from the chemical shifts of similar atoms in a corresponding linear alkane 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 alkane n.

3. 2. The comparison of similar mean differential spectral parameters \(\bar{Nn-i}\) (or \(\Delta C^{Nn}_{i}\)) 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 \(n \rightarrow Nn\)) does not extend more than next four carbon atoms after a branched chain atom (C-N). For example, in complete 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 \(C^{N-3}\)), i.e., only for above \(\text{decarbonic 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, i.e, 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.
The mean values of differential spectral parameter $Nn-i$ ($N = 2, 3, 4, 5$) of N-methylalkanes $2n$, $3n$, $4n$ and $5n$.

<table>
<thead>
<tr>
<th>Number of compounds $Nn$ families</th>
<th>The mean DSP values ($Nn-i$ or $\delta^{13}C_{Nn}$) in ppm of specified number of “i-type” carbon atoms</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[C-(N-4)]$</td>
<td>$[C-(N-3)]$</td>
</tr>
<tr>
<td>2n</td>
<td>-</td>
</tr>
<tr>
<td>3n</td>
<td></td>
</tr>
<tr>
<td>4n</td>
<td>-</td>
</tr>
<tr>
<td>5n</td>
<td>+0.1</td>
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</tbody>
</table>

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 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 $Nn-i$: $Nn-[N] = +3.25 \pm 0.05$ ppm; $Nn-[N'] = +5.7 \pm 0.05$ ppm; $Nn-[N+1] = +7.55 \pm 0.05$ ppm; $Nn-[N+2] = -2.45 \pm 0.05$ ppm; $Nn-[N+3] = +0.45 \pm 0.05$ ppm; $Nn-[N+4] = +0.1 \pm 0.05$ 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 $Nn-[N+1] = +7.55 \pm 0.05$ ppm). The remaining carbon atoms of the starting 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 dicarbonylic fragment $[C-N] - [C-N']$). For example, $2n-1 = +8.6$ ppm versus $Nn-[N+1] = +7.55 \pm 0.05$ ppm; $2n-2 = 5.4$ ppm versus $Nn-[N] = +3.25 \pm 0.05$ ppm; $2n-2' = 8.6$ ppm versus $Nn-[N'] = +5.7 \pm 0.05$ 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 $4m-B-2$; $4m-B-3$).
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 \( (\delta_i) \) of hypothetical infinitely long chain alkanes \( (n_v) \), which are denoted as \( n_v-B-i_m \). The value of this parameter is the same for all carbon atoms of the studied molecule \( n_v-B-i_m = 29.75 \text{ ppm} \). In the second line we present the abovementioned sum [5] of two increment values \( \Delta B-i = (\Delta\delta_i) + (\Delta B-i_{\text{fin.}}) \) 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: \( Nn-B-i = n_v-B-i_m + \Delta B-i_{\text{start.}} + \Delta B-i_{\text{fin.}} + Nn-i \). 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: \( [(Nn-B-i)_{\text{calc.}} - (Nn-B-i)_{\text{exp.}}] \), which are less than 0.1 ppm, painted red.

\[
\begin{array}{lcccccc}
n_v-B-i_m(\delta_i), \text{ ppm} & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 \\
\Delta B-i_{\text{start.}} + \Delta B-i_{\text{fin.}}, \text{ ppm} & -15.65 & -7.05 & -15.65 & +1.95 & +1.95 & -7.05 & -15.65 \\
\end{array}
\]

**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 ($2l$-$B$-$i$)$_{\text{calc,}}$ and experimental ($2l$-$B$-$i$)$_{\text{exp.}}$ results (top line) does not exceed the absolute value of 0.1 ppm.

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

$n_v$-$B$-$i_m$, 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 29.75

$\Delta B$-$i$, ppm -15.65 -7.00 -15.65 +2.25 -0.30 -0.05 0 -0.05 -0.30 +2.25 -7.00 -15.65

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

$Nn$-$i$ and/or $\Delta B$-$i$, 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

$(Nn$-$B$-$i$)$_{\text{calc.}}$, 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

$(Nn$-$B$-$i$)$_{\text{exp.}}$, ppm 30.08 29.86 29.79

Difference: $[(Nn$-$B$-$i$)$_{\text{calc.}}$ - $(Nn$-$B$-$i$)$_{\text{exp.}}$] -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 $(3l$-$B$-$i$)$_{\text{exp,}}$ parameters (where $i = 2, 7$) the difference between the calculated $(3l$-$B$-$i$)$_{\text{calc,}}$ and experimental $(3l$-$B$-$i$)$_{\text{exp.}}$ results (top line) does not exceed the absolute value of 0.1 ppm.

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

$n_v$-$B$-$i_m$, 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 29.75

$\Delta B$-$i$, ppm -15.65 -7.00 +2.25 -15.65 -0.30 -0.05 0 -0.05 -0.30 +2.25 -7.00 -15.65

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

$Nn$-$i$ and/or $\Delta B$-$i$, ppm -2.45 +7.55 +3.25 +5.7 +7.55 -2.45 +0.45 +0.1 0 0 0 0 0

$(Nn$-$B$-$i$)$_{\text{calc.}}$, 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

$(Nn$-$B$-$i$)$_{\text{exp.}}$, ppm 29.64 29.85

Difference: $[(Nn$-$B$-$i$)$_{\text{calc.}}$ - $(Nn$-$B$-$i$)$_{\text{exp.}}$] +0.66 -0.05

Example 4.
Calculation of all base spectral parameters $4m$-$B_i$ of longchain representative of the 4-methylandalkane family – 4-methyldeodecane $4m$ 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 $(4m-B_i)_{\text{exp}[6]}$ parameters (where $i = 5, 6, 7$) the difference between the calculated $(4m-B_i)_{\text{calc}}$ and experimental $(4m-B_i)_{\text{exp}}$ results (top line) does not exceed the absolute value of 0.1 ppm.

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

$\begin{array}{cccccccccccc}
 n_{\text{e}}B_{i_{\text{m}}}, \text{ ppm} & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 \\
\Delta B_i, \text{ ppm} & -15.65 & -7.00 & +2.25 & -0.30 & -15.65 & 0 & 0 & 0 & -0.05 & -0.30 & +2.25 & -7.00 & -15.65 \\
\end{array}$

$\begin{array}{cccccccccccc}
 C^1H_3^1-C^2H_2^2-C^3H_2^3-C^4H_4^4-(C^4H_4^4)_5-C^5H_5^5-C^6H_6^6-C^7H_7^7-C^8H_8^8-C^9H_9^9-C^{10}H_{10}^{10}-C^{11}H_{11}^{11}-C^{12}H_{12}^{12} \\
 Nn-i & \text{and/or } & \Delta B_i, \text{ ppm} & +0.45 & -2.45 & +7.55 & +3.25 & +5.7 & +7.55 & -2.45 & +0.45 & +0.1 & 0 & 0 & 0 \\
(Nn-B_i)_{\text{calc}}, \text{ ppm} & 14.55 & 20.30 & 39.55 & 32.7 & 19.8 & 37.3 & 27.3 & 30.2 & 29.80 & 29.45 & 32.00 & 22.75 & 14.10 \\
(Nn-B_i)_{\text{exp}}, \text{ ppm} & 20.29 & 19.74 & 27.26 & 30.22 & 37.29 & 30.22 & 27.26 & 29.87 & 29.54 & 32.11 & 22.83 & 14.14 \\
\end{array}$

Difference: $[(Nn-B_i)_{\text{calc}} - (Nn-B_i)_{\text{exp}}] = \begin{array}{ccccccc}
 +0.10 & +0.06 & +0.04 & -0.02 \\
 +0.56 & -0.08 & +0.02 & -0.49 & +0.01 & -2.92 & +2.89 & -0.07 & -0.09 & -0.11 & -0.08 & ; \end{array}$

**Example 5.**

Calculation of all base spectral parameters $4j$-$B_i$ of midchain (almost longchain) representative of the 4-methylandalkane 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 $(4j-B_i)_{\text{exp}[6]}$ 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.

$\begin{array}{cccccccccccc}
 n_{\text{e}}B_{i_{\text{m}}}, \text{ ppm} & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 & 29.75 \\
\Delta B_i, \text{ ppm} & -15.65 & -7.00 & +2.25 & -0.30 & -15.65 & -0.10 & -0.30 & +2.25 & -7.00 & -15.65 & 0 \\
\end{array}$

$\begin{array}{cccccccccccc}
 C^1H_3^1-C^2H_2^2-C^3H_2^3-C^4H_4^4-(C^4H_4^4)_5-C^5H_5^5-C^6H_6^6-C^7H_7^7-C^8H_8^8-C^9H_9^9 \\
 Nn-i & \text{and/or } & \Delta B_i, \text{ ppm} & +0.45 & -2.45 & +7.55 & +3.25 & +5.7 & +7.55 & -2.45 & +0.45 & +0.1 & 0 & 0 & 0 \\
(Nn-B_i)_{\text{calc}}, \text{ ppm} & 14.55 & 20.30 & 39.55 & 32.7 & 19.80 & 37.2 & 27.0 & 32.45 & 29.85 & 14.10 \\
(Nn-B_i)_{\text{exp}}, \text{ ppm} & 32.67 & 32.45 \\
\end{array}$
Difference: \[ ((Nn-B-i)_{\text{calc}} - (Nn-B-i)_{\text{exp}}) \]

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Example 6.

Calculation of all base spectral parameters 5j-B-i of sole representative of the 5-methylalkane family – symmetrical midchain (almost longchain) 5-methyliononane 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.

\[ n_{x-B-i_{\text{in}}} \text{, ppm} \]

\[ +0.1 \text{ ppm} \]

\[ \Delta B-i_{\text{, ppm}} \]

\[ -15.65 \text{ ppm} \]

\[ n_{x-B-i_{\text{m}}} \text{, ppm} \]

\[ 29.75 \text{ ppm} \]

\[ \text{C}^1 \text{H}^3 \text{—} \text{C}^2 \text{H}^2 \text{—} \text{C}^3 \text{H}^3 \text{—} \text{C}^4 \text{H}^4 \text{—} \text{C}^5 \text{H}^5 \text{—} (\text{C}^5 \text{H}^5) \text{—} \text{C}^6 \text{H}^6 \text{—} \text{C}^7 \text{H}^7 \text{—} \text{C}^8 \text{H}^8 \text{—} \text{C}^9 \text{H}^9 \text{—} \]

\[ \text{Nn-i and/or } \Delta B-i_{\text{, ppm}} \]

\[ +0.1 \text{ ppm} \]

\[ (Nn-B-i)_{\text{calc}}_{\text{, ppm}} \]

\[ 14.2 \text{ ppm} \]

\[ (Nn-B-i)_{\text{exp}}_{\text{, ppm}} \]

\[ 14.21 \text{ ppm} \]

Difference: \[ ((Nn-B-i)_{\text{calc}} - (Nn-B-i)_{\text{exp}}) \]

|                | -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 \[ ((Nn-B-i)_{\text{calc}} - (Nn-B-i)_{\text{exp}}) \] 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 \[ ((Nn-B-i)_{\text{calc}} - (Nn-B-i)_{\text{exp}}) \] 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 \[ (2f-B-2)_{\text{calc}} - (2f-B-2)_{\text{exp}} \], example N1] to +0.6 ppm [for difference \[ (2l-B-3)_{\text{calc}} - (2l-B-3)_{\text{exp}} \], example N3]. In this interval we do not include the value of the parameters \[ ((2n-B-2')_{\text{calc}} - (2n-B-2')_{\text{exp}} \] [where \( n = 6 \text{ (2f)} \) and \( n = 11(2l) \)], since by definition parameters \[ (2n-B-1)_{\text{calc}} - (2n-B-1)_{\text{exp}} \] and \[ (2n-B-2')_{\text{calc}} - (2n-B-2')_{\text{exp}} \] 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 \[ (2f-B-1)_{\text{calc}} - (2f-B-1)_{\text{exp}} \] and \[ (2f-B-2')_{\text{calc}} - (2f-B-2')_{\text{exp}} \] is equal to: \( (-1.06) + (-2.91) / 2 = \approx -1.99 \text{ ppm} \), 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 \[ ((Nn-B-i)_{\text{calc}} - (Nn-B-i)_{\text{exp}}) \]. A possible exception is the case of shown in Example N 3, where parameter \[ |(3l-B-2)_{\text{calc}} - (3l-B-2)_{\text{exp}}| = 0.66 > |(3l-B-2)_{\text{calc}} - (3l-B-2)_{\text{exp}}| = 0.45 \]. 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 \[ (3l-B-7)_{\text{calc}} - (3l-B-7)_{\text{exp}} \] enhances its value (from +0.16 to -0.05 ppm). We believe that this improvement of good predictable difference \[ (3l-B-7)_{\text{calc}} - (3l-B-7)_{\text{exp}} \] is more significant than the degradation of the conjugate parameter \[ (3l-B-2)_{\text{calc}} - (3l-B-2)_{\text{exp}} \], 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 $\Sigma Nn\cdot i$) 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 $\Sigma Nn\cdot i$ (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 $Nn\cdot i$ of next decarboxonic 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 $\Sigma 3n\cdot i$ 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 $\Sigma Nn\cdot i$ we assume to use abovementioned general mean differential spectral parameters values $Nn\cdot i$ 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 $Nn\cdot i$ 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 $\Sigma Nn\cdot i$ are obtained, when we use individual (not general) for each family mean differential spectral parameters $Nn\cdot i$. The values of mean differential spectral parameters $Nn\cdot i$ for each carbon atoms in starting side and four atoms 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 $\Sigma Nn\cdot i$ for all four monomethylalkanes families, using individual for each family mean differential spectral parameters $Nn\cdot i$.

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

Similarly let’s calculate:

a) the ”aggregated” spectral changes $\Sigma 3n\cdot i$ 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 $\Sigma 4n\cdot i$ 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 $\Sigma 5j\cdot i$ for 10 carbon atoms of 5-methylmononane - 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 $\Sigma Nn\cdot i$ values leads us to the next conclusions.

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

2) The values of the integral parameters $\Sigma Nn\cdot i$ decreases in the row $\Sigma 2n\cdot i > \Sigma 3n\cdot i > \Sigma 4n\cdot i$, and then practically stabilizes: $\Sigma 4n\cdot i \approx \Sigma 5n\cdot i$. 
3) The integral parameter $\sum 2n-i$ approximately one and a half times more than the other three similar parameters ($\sum 3n-i$, $\sum 4n-i$ and $\sum 5n-i$).

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 monomethylalkanes Nn, accompanied by a significant downfield shift of “aggregated” signs $\sum Nn-i$ of remaining and newly formed types carbon atoms.

The ending

It is of interest to compare the relative integral parameters $\sum Nn-i$ 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 $\sum Nn-i$ 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 ($^{13}$CN$^N$H$^N$) 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 $\sum Nn-i$ in the protonic spectrum decreases from value ($\sum Nn-i = -65 \pm 50$ mlrd.) for monomethylalkanes 2n family (when N = 2) to value ($\sum Nn-i = -350 \pm 30$ mlrd.) for monomethylalkanes Nn families (when N = 3, 4, 5). A similar situation occurs with carbonic $^{13}$C NMR spectra integral parameters $\sum Nn-i$. For them, as shown above in Section 3.4., a positive value of integral parameters $\sum Nn-i$ in the carbonic spectrum decreases from value ($\sum Nn-i = +28.4$ ppm) for monomethylalkanes 2n family (when N = 2) to value ($\sum Nn-i = +21 \pm 1.0$ 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 $\sum Nn-i$.

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

3. The values of the sum parameter ($\sum Nn-i = +28.4$ 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) ($\sum Nn-i = +21 \pm 1.0$ ppm).

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References


