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PECULIARITIES OF NMR ^{1}H AND ^{13}C SPECTRA OF ALKYL GROUPS IN FUNCTIONALIZED LINEAR ALKANES OF THE GENERAL FORMULA $CH_3(CH_2)_MY$

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Abstract. Literature data of NMR ^{1}H and ^{13}C spectra of linear alkanes X–$(CH_2)_n$–Y (**I**), (where X = H; Y – 38 different substituents, including H and CH_3) were considered. The new universal way of estimating the chemical shifts values of the methylene groups (δ^H_{CH2} = = δ^H_i, δ^C_{CH2} = δ^C_i, i = 1–38) in **I** was proposed. The concept of it considers changes in the values δ^H_i and δ^C_i of each methylene groups in **I** (called as increments $\Delta\delta^H_i$ and $\Delta\delta^C_i$) as a result of conversion to **I** of a hypothetic alalkane –$(CH_2)_k$–$(CH_2)_n$–$(CH_2)_l$– (**II**) by replacing infinitely long fragments –$(CH_2)_k$– and –$(CH_2)_l$– of it with the substituents X and Y. Increments $\Delta\delta^H_i$ and $\Delta\delta^C_i$ for all substituent types were calculated and tabulated. The proposed method allows to calculate the δ^H_i and δ^C_i parameters for the unpublished NMR ^{1}H and ^{13}C spectra of long- and medium-chain compounds **I.** The example of calculations was given.

Keywords: NMR ^{1}H and ^{13}C spectra, *l*-substituted linear alkanes, long-, medium- and short-chain compounds, basic spectral parameter, increment.

1. Introduction

One of the most important and intriguing problems of natural philosophy is an interaction between the substance structure and its properties. To our mind the final solution of this problem is impossible. As our knowledge about new properties develops, the question concerning their dependence on structure (subatomic, atomic, molecular, supramolecular, *etc*.) arises again and again.

When studying the interaction of the substance placed inside the magnetic field with wideband electromagnetic radiation of radio-frequency region the selective absorption of definite frequencies was observed, *i.e.* spectral absorption by atomic nuclei of the molecules which are parts of the substance structure. In such a way the new scientific direction – spectroscopy of nuclear-magnetic resonance (NMR) originated. The absorption spectra of carbon and hydrogen atoms nuclei (NMR ^{13}C and NMR ^{1}H, respectively) were found to be the most important for the organic chemistry.

Proton spectra NMR were used in the organic chemistry from the beginning of fifties of the last century. And from that moment the investigators put a question: what is the dependence between values of a proton chemical shift (d^H_i) and investigated compound structure? Series of empirical correlations were found which are now in all textbooks; the typical absorption areas were determined for the most important types of protons. As a rule, the empirical correlations were not connected with each other and mainly applied to the protons of carbon α-atom bonded with the substituent. The studies of other protons were not so elaborated. Moreover, some determined correlations had not well-defined theoretical explanations. For example, in ethylhalogenides CH_3–CH_2–Hal the values d^H_{CH2} of methylene group protons depend in direct proportion on the electro-negativity of halogen atom and for the methyl protons d^H_{CH3} this proportion is inverse.

Since sixties NMR ^{13}C spectra were also used in the organic chemistry. The same as for proton spectra, the typical areas of some carbon atoms absorption as well as empirical correlations were found. However systematic investigations concerning the dependence between spectral parameters and substances structure were not carried out.

2. Experimental

2.1. The Aim of Investigation

We decided to bridge this gap and choose a traditional way of solution – from the simple problem to the complex one. Monosubstituted nonbranched alkanes (especially for those cases when the substituent was at the beginning of the chain) and the simplest aromatic compounds (benzene monosubstituted derivatives) were examined as the simplest ones. The spectral parameters NMR ^{1}H and ^{13}C were chosen as investigation objects. The aim was to investigate **all spectral changes occurring in NMR ^{1}H and ^{13}C spectra** at the introduction of various substituents in the molecule of reference substance – nonsubstituted nonbranched alkane. In our work we try **to understand the logic of signals formation** for all hydrogen and carbon atoms in NMR ^{1}H and ^{13}C spectra of investigated compounds. For this purpose we made an attempt to define the main factors affecting the basic spectral parameters in NMR ^{1}H and ^{13}C spectra of organic compounds, *i.e.* the values of δ^H_i and δ^C_i chemical shifts of corresponding atoms nuclei. According to the purpose we selected rows of investigated compounds. If the regular character of the nuclei absorption signals is observed depending on the compound structure within the rows, the conclusion about the possible presence of regularity during parameters δ^H_i and δ^C_i formation was done. The first part of our work is determination of main factors affecting δ^H_i and δ^C_i parameters in NMR ^{1}H and ^{13}C spectra of the simplest aliphatic compounds – linear aliphatic molecules, containing functional end-group Y[1].

For this purpose we chose definite rows of compounds of the general formula $CH_3(CH_2)_m$-Y(**I**), containing 38 substituents Y which are the most important to our mind and then examined two types of spectra. It is advisable to divide the investigated alkyl fragment into two virtual parts: internal and external. The internal part is carbon skeleton of the molecule; the external one is sum-total of hydrogen atoms connected with carbon atoms.

$$\overset{\delta^H_i,\ \delta^C_i}{CH_3\text{–}(CH_2)_m\text{–}Y} \leftrightarrow \overset{\delta^H_i,\ \delta^C_i}{H\text{–}(CH_2)_n\text{–}Y}$$

I, $n = m + 1$

where Y = H– (**1**); CH_3– (**2**); $(CH_3)_2CH$– (**3**); $(CH_3)_3C$– (**4**); CH_2=CH– (**5**); C≡CH– (**6**); C_6H_5– (**7**); N≡C– (**8**); O=CH– (**9**); O=C(CH_3)– (**10**); O=C(C_6H_5)– (**11**); O=C(NH_2)– (**12**); O=C(OH)– (**13**); O=C(OCH_3)– (**14**); O=C(OC_2H_5)– (**15**); O=C(Cl)– (**16**); NH_2– (**17**); NHR– (**18**); NH(CH_3)– (**19**); N$(CH_3)_2$– (**20**); NR_2– (**21**); NR(CH_3)– (**22**); NO_2– (**23**); HO– (**24**); RO– (**25**); O=C(H)–O– (**26**); O=C(CH_3)–O– (**27**); O=C(C_3H_7)–O– (**28**); O=C(C_6H_5)–O– (**29**); O=C(C_6H_5)–C(=O)–O– (**30**); $O_2S(C_6H_4$–CH_3–p)–O– (**31**); HS– (**32**); RS– (**33**); F– (**34**); Cl– (**35**); Br– (**36**); I– (**37**), $(C_2H_5O)_2CH$– (**38**).

[1] Functional substituent in the formula (I) purposely denoted as "Y" in order to avoid confusion possible while using symbols X, V and I which are used as numbers of Roman alphabet.

We made the attempts to determine the main **factors** affecting the chemical shifts values of hydrogen and carbon nuclei (d^H_i and δ^C_i) in NMR ^{1}H and ^{13}C spectra of compounds (**I**) in both contours of alkyl fragment. The second task was to **determine the importance** of every investigated factor. To our mind the most evidence factor is the effect of the **substituent Y nature** on the basic spectral parameters d^H_i and δ^C_i of those carbon and hydrogen atoms which form both counters of alkyl fragment of molecule $CH_3(CH_2)_m$–Y and location of these atoms in the chain.

2.2. Investigation Procedure

There are a lot of empirical correlations to calculate the d^H_i and δ^C_i parameters in the linear alkanes. We do not consider them here because they are inaccurate and have not theoretical models.

The important question arises: which standards may be used to calculate the changes in spectra at the substituent introduction into the alkane molecule? Earlier nobody attended to this question. For example, in the textbook [1] the changes of 1-nitropropane spectrum relatively to nonsubstituted n-propane spectrum are described. Hence, *n*-butane should be the reference substance for nitrobutane, *etc*. But it is impossible then to find the general standard for all linear substituted alkanes. We propose another way.

To study the dependencies of experimental values d^H_i and δ^C_i (i = 1–n) for all methylene groups in the compounds **I** upon their positions in the linear alkyl chain relatively to the substituent Y we suggest the intermediate use of hypothetical model – alkane linear molecule with infinitely long carbon chain by the general formula (**II**). The coefficients k and l in the compound **II** are suggested to be infinitely large, and coefficient m is a finite quantity corresponding to the coefficient m in the molecules **I**.

With great probability we may assume that all carbon and hydrogen atoms of every methylene groups of the alkyl chain in the compound **II** (including m atoms of methylene groups) are in the same chemical surroundings. Therefore, they have the same values of the basic spectral parameter d^H_i and δ^C_i, denoted as $\delta^H_{hyp.}$ and $\delta^C_{hyp.}$, respectively.

$$\overset{\delta^H_k,\ \delta^c_k}{-(CH_2)_k-}\overset{\delta^H_n,\ \delta^c_n}{(CH_2)_n-}\overset{\delta^H_l,\ \delta^c_l}{(CH_2)_l-}$$

II

$$k = l = \infty$$

$$\delta^c_k = \delta^c_l = \delta^c_n = \delta^c_{hyp.}$$

$$\delta^H_k = \delta^H_l = \delta^H_n = \delta^H_{hyp.}$$

The basis of the suggested conception is an assumption that during transformation of the hypothetical molecule **II** into the real molecule **I** it is necessary to perform hypothetical operations which will change the structure **II** (*i.e.* will disturb molecule **II**) and change the $\delta^H_{hyp.}$ and δ^C_{hyp} parameters. The infinitely long methylene fragment $–(CH_2)_k–$ will be changed for the hydrogen atom on the left side of the molecule **II**, and fragment $–(CH_2)_l–$ on the right side will be changed for the functional group Y. Thus the transfer from the molecule **II** to the molecule **I** will be finished (Fig. 1).

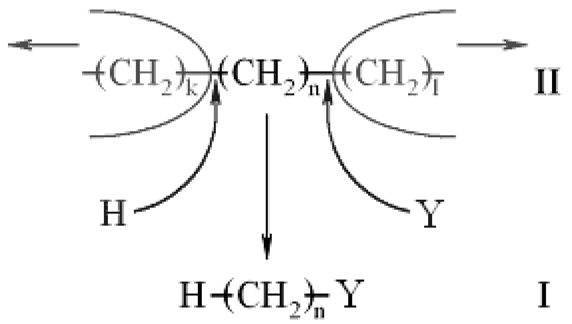

Fig. 1. The hypothetic transformation of virtual alkane **II** to the investigated compounds **I**

All δ^H and δ^C values were taken from more reliable (to our mind) literature sources: site of National Institute of Advanced Industrial Science and Technology (Japan) [2] and internet-atlas of ALDRICH firm [3]. The choice of literature sources was grounded on the observation of their reliability and compatibility, criteria of which are discussed in [4]. To discuss the peculiarities of the basic spectral parameters δ^H and δ^C we took only values obtained during spectrum recording in deuterochloroform as a solvent. Spectra obtained in other solvent, *e.g.* DMSO-d6, D_2O *etc.*, we do not examine here.

The parameters $\delta^{H}_{i}{}^{[2]}$, given in [2] were obtained using instruments with different frequency: low-frequency (90 MHz) and high-frequency (300 or 400 MHz). In those cases when both values δ^H_i are given and there is a difference between them, we used only "high-frequency" parameter. "Low-frequency" parameter was used only in the absence of "high-frequency" value. NMR ^{13}C spectra given in [2] were obtained using low-frequency instruments (15, 22.5 and 25 MHz) or high-frequency instruments (50 and 100 MHz). All spectra given in [3] were obtained using high-frequency instrument (300 MHz for NMR ^1H and 75 MHz for NMR ^{13}C spectra). The drawback of NMR ^{13}C spectra obtained by low-frequency instruments is uncertainty of signal values in the region of 29.5–30.0 MHz. Very often several signals have the same value. Usually the "high-frequency" spectra are without this drawback. We assume them as "more reliable" in those cases when different values were obtained by low- and high-frequency instruments for the same signals.

In the spectra given in [2] the author's attribution of the signals to the absorption of particular nuclei of hydrogen and carbon atoms is stated. In most cases we agree with the authors, otherwise we suggest our own attribution (more correct, to our mind). The authors of data represented in [3] do not give their own attribution of spectra signals; therefore we do this by ourselves. Usually the data from [2] coincide with the data from [3] for different compounds[2].

We estimate the inaccuracy of measurements of NMR ^1H spectra as ± 0.02 ppm. Henceforth all values of δ^H_i parameters are rounded to the nearest number divisible by 0.01 ppm, whilst sometimes authors [2] present the results with the accuracy of 0.001 ppm. The accuracy of δ^C_i values given in [2] and [3] we estimate as 0.05 ppm, therefore further δ^C_i values we round to the number divisible by 0.05 ppm.

3. Results and Discussion

3.1. Compounds of the General Formula (I) with Long Alkyl Chain ("Long-Chain" Compounds I)

3.1.1. Used symbols

As mentioned above we assume that all carbon and hydrogen atoms of alkyl chain in the hypothetic alkane **II** (including *m* atoms of methylene groups) are located in the same chemical surrounding. Therefore they have the same values of basic spectral parameter δ^H_i and δ^C_i denoted respectively as δ^H_{hyp} and δ^H_{hyp}. Obviously that due to the transformation of the hypothetic alkane **II** to the real compound **I** the value δ^H_i and δ^C_i of all (or some) carbon and hydrogen atoms is changed in $–(CH_2)_m–$ fragment.

These changes are mainly applied to *r* carbon and hydrogen atoms in $(CH_2)_n$ fragment which are closer to the point where $H(CH_2)_k$ fragment in **II** is exchanged for the hydrogen atom (so called "methyl" end of the alkyl fragment in **I**). We denoted the δ^H_i and δ^C_i parameters of *r* methylene groups as δ^H_r and δ^C_r. The same situation takes place during the substitution of $H(CH_2)_l–$ fragment in **II** for Y group on the right (functionalized) end for *s* atoms of $(CH_2)_n$ fragment in **I**, for which $\delta^H_i = \delta^H_s$ and $\delta^C_i = \delta^C_s$. Hence, in order to avoid the superposition of two different "disturbances", the length of $H(CH_2)_n–$ chain in the molecule **I** should be not less than the total amount of

[2] Sometimes the difference between data from [2] and [3] is great.

carbon atoms $r+s$. If the number of carbon atoms (n) in the compounds **I** exceeds the sum of $r+s$ coefficients by one, we call such compounds as "long-chain" ones. For these compounds the inequality (1) must take place:

$$n > r + s \qquad (1)$$

The "additional" methylene groups in the amount of "t", which do not belong to r and s, we call "middle" in the long-chain compounds. Hence, the inequality (1) is equivalent to the inequality $t \geq 1$. The values of basic parameters δ^H_i of hydrogen atoms t and δ^C_i of carbon atoms t of "middle" methylene groups in alkyl chains are denoted as δ^H_t and δ^H_t respectively. Hence, at least one "middle" methylene group (*i.e.* $t \geq 1$) with the parameters $\delta^H_i = \delta^H_t$ and $\delta^C_i = \delta^C_t$ must be in the "long-chain" compounds **I**. **We assume the value of the mentioned parameter is equal to the virtual parameter δ^H_{hyp} (δ^C_{hyp}), *i.e.* $\delta^H_{hyp.} = \delta^H_t$ and $\delta^C_{hyp.} = \delta^C_t$.**

$$\delta^H_r, \delta^C_r \quad \delta^H_t, \delta^C_t \quad \delta^H_s, \delta^C_s$$
$$H\text{-}(CH_2)_r\text{–}(CH_2)_t\text{–}(CH_2)_s\text{–}Y$$
I, $n = r + s + t$

"Long-chain" molecules **I**

The differences between parameters of "end" methylene groups (δ^H_r, δ^H_s, δ^C_r and δ^C_s) and parameters of middle methylene groups (δ^H_t and δ^C_t) are caused by "molecule disturbance" taking place first during the transformation from **II** to **I**. The values of the mentioned differences (so called "increments") are determined by differential spectral parameters $\Delta\delta^H_r$ and $\Delta\delta^H_s$ ($\Delta\delta^C_r$ and $\Delta\delta^C_s$) and equal to the difference between real (experimental) values of the basic parameter δ^H_i (or δ^C_i) in the fragment $(CH_2)_m$ of the molecule **I** and constant value δ^H_t (δ^C_t). Increments $\Delta\delta^H_r$, $\Delta\delta^H_s$, $\Delta\delta^C_r$ and $\Delta\delta^C_s$ are calculated by the formulas (2) and (3):

$$\Delta\delta^H_r = \delta^H_r - \delta^H_{hyp}; \quad \Delta\delta^C_r = \delta^C_r - \delta^C_{hyp} \qquad (2)$$
$$\Delta\delta^H_s = \delta^H_s - \delta^H_{hyp}; \quad \Delta\delta^C_s = \delta^C_s - \delta^C_{hyp} \qquad (3)$$

3.2. Linear Alkanes of the General Formula 2 (Y = CH_3 in Formula I)

The nearest compounds modeling the spectral properties of hypothetical alkane with infinitely long chain **II** are linear alkanes with the chain length more than 11 (see below) carbon atoms; it may be obtained *via* transformation of hypothetical compound **II** by the substitution of the second infinitely long fragment $H(CH_2)_l$– for one more hydrogen atom, *i.e.* at Y = H (or methyl group, *i.e.* at Y = CH_3). So the whole class of linear alkanes comes within the type of compounds of the general formula **I**. Depending upon the value of the substituent Y, these compounds may be denoted by bold Arabic **1** (at Y = H) or **2** (at Y = CH_3). Further we'll denote them as **1** for the uniformity. They contain 2 methyl and m methylene groups. So the number of carbon atoms (n) in the long-chain alkanes **1** is $n = m+2$, taking into account the presence of two methyl groups at both ends of the chain. Therefore, the linear alkanes **1** with the chain length of more than 11 carbon atoms, *i.e.* starting from undecane (n = 11, m = 9) and higher are denoted by the general term "long-chain alkanes" (see below).

In accordance with above-mentioned definitions, for the inclusion of investigated compound to the group of "long-chain" compounds the value of the parameter n depends upon accepted by us values of r and s parameters. The number of carbon atoms s depended on the substituent Y nature. Therefore the minimum size of "long-chain" compound chain may be different for different types of the compound **I**. Moreover, the parameters r and s determined for NMR ^{1}H spectra (see below) are considerably less than for NMR ^{13}C spectra. It is the reason for terminology discrepancy concerning external and internal contours of the molecules **I**, including alkanes **1.** For example, in benzoic acid esters of linear alcohols [5] we intuitively called as "long-chain" the alkoxyl groups with 4 and more carbon atoms in the chain (i.e. starting from butyl group) though such linear fragments should be longer from the standpoint of NMR ^{13}C spectra. Now our intuitive determinations are confirmed (see below).

To our mind it is advisable to examine here spectral parameters δ^H_i, δ^C_i, $\Delta\delta^H_i$ and $\Delta\delta^C_i$ for **all** n carbon atoms of every linear alkane **1** including methyl end-atoms C^1 and C^n. The latter ones imprescriptibly belong to the alkyl chain in the compounds **1**, though they are not declared above as methylene groups of the fragment $–(CH_2)_m–$.

Since the values $\Delta\delta^H_r$ ($\Delta\delta^C_r$) and $\Delta\delta^H_s$ ($\Delta\delta^C_s$) are the measure of changes of the molecule disturbance during conversion of hypothetical structure **II** to the real molecules **I**, in the spectra of long-chain alkalnes **1** (Y = H) due to the molecule symmetry the numerical values of basic spectral parameters δ^H_i (δ^C_i) are equal by pairs [*i.e.* $\delta^H_1 = \delta^H_n$ ($\delta^C_1 = \delta^C_n$), $\delta^H_2 = \delta^H_{n\text{-}1}$ ($\delta^C_2 = \delta^C_{n\text{-}1}$), *etc.*]. Hence, in alkalnes **1** corresponding increments are equal as well, *i.e.* $\Delta\delta^H_{r,1} = \Delta\delta^H_{s,1}$ and $\Delta\delta^C_{r,1} = \Delta\delta^C_{s,1}$. Their absolute values decrease as they approach to the middle of the chain.

While analyzing the NMR ^{13}C spectra of long-chain alkanes **1** from $C_{11}H_{24}$ to $C_{38}H_{78}$ given in [2, 3] we found that δ^C_t values of the middle methylene groups are constant within the limits of measurement error and equal to 29.75 ± 0.10 ppm[3]. The important assumption is that virtual value $\delta^C_{hyp.}$ in the hypothetical molecule **II** is numerically equal to δ^C_t in long-chain alkanes **1**, *i.e.* **$\delta^C_{hyp} = \delta^C_t$ = 29.75 ppm.** We found that (as we expect) the

[3] We fixed just upon this value. The alternative value may be δ^C_t = 29.80 ppm.

absolute values of increments $\Delta\delta^C_r = \Delta\delta^C_s$ gradually decrease to the zero values as they approach to the middle of the chain. Moreover, for only 5 extreme carbon atoms at each end of the chain (*i.e.* at $r = s = 5$) there is a difference between founded values and $\delta^C_t = 29.75$ ppm equal to 0.05 ppm (or more) by absolute value. Therefore, according to inequality (1) we determined **linear alkanes starting from undecane $C_{11}H_{24}$ as long-chain alkanes** because 11 = 5 + 5 + 1. As mentioned above in all spectra of long-chain alkanes **1** the numerical values of every 5 types of δ^C_r (δ^C_s) are equal in pairs, *i.e.*: $\delta^C_1 = \delta^C_n$, $\delta^C_2 = \delta^C_{n\text{-}1}$, $\delta^C_3 = \delta^C_{n\text{-}2}$, $\delta^C_4 = \delta^C_{n\text{-}3}$ and $\delta^C_5 = \delta^C_{n\text{-}4}$. The experimental values [2, 3], averaged spectral parameters δ^C_r (δ^C_s) and δ^C_t for long-chain alkanes **1** which were used for the calculation by formula (4) and calculated increments $\Delta\delta^C_r$ ($\Delta\delta^C_s$) are represented in Table 1. All values are rounded to a number divisible by 0.05 ppm.

$$\Delta\delta^C_r = \delta^C_r - \delta^C_t = \Delta\delta^{C,1}_s = \delta^{C,1}_s - \delta^C_t \quad (4)$$

Table 1

Average values of long-chain alkanes 1 $\Delta\delta^C_r$ increments

Carbon atom number in the chain	C-1 (C_n)	C-2 (C_{n-1})	C-3 (C_{n-2})	C-4 (C_{n-3})	C-5 (C_{n-4})	C-6 (C_{n-5})
Averaged experimental parameter δ^C_r (δ^C_s), ppm	**14.10**	**22.75**	**32.00**	**29.45**	**29.70**	**29.75**
Averaged experimental parameter δ^C_t in alkanes **1**, accepted to be equal to the virtual parameter $\delta^C_{hyp.}$ in **II**, ppm	29.75	29.75	29.75	29.75	29.75	29.75
Averaged increment $\Delta\delta^C_r$ ($\Delta\delta^C_s$), ppm	**-15.65**	**-7.00**	**+2.25**	**-0.30**	**-0.05**	**0.00**

Here we present averaged values of the basic spectral parameters δ^C_r (δ^C_s) in the long-chain alkanes **1** taking n-dodecane ($C_{12}H_{26}$) as an example:

$$\underset{14.10}{C^1H_3}-\underset{22.75}{C^2H_2}-\underset{32.00}{C^3H_2}-\underset{29.45}{C^4H_2}-\underset{29.70}{C^5H_2}-\underset{29.75}{(CH_2)_2}-\underset{29.70}{C^{n-4}H_2}-\underset{29.45}{C^{n-3}H_2}-\underset{32.00}{C^{n-2}H_2}-\underset{22.75}{C^{n-1}H_2}-\underset{14.10}{C^nH_3}$$

In NMR^{1}H spectra given in [2, 3] for the long-chain linear alkanes **1** starting from C_6H_{14} (see below) to $C_{38}H_{78}$ the absorption of middle methylene groups is shown as broadened singlet signal (so called "methylene hump"). The value of its center may be accepted as 1.27±0.02 ppm within the error range[4]. Increments **$\Delta\delta^H_r$ and $\Delta\delta^H_s$, exceeding the value of 0.07 ppm** by absolute value[5], were determined in alkanes **1** for only hydrogen atoms of methyl groups (*i.e.* only for $\Delta\delta^H_1$ and $\Delta\delta^H_n$; at $r = s = 1$). The absolute values of other increments (starting from $r = s = 2$) have "insufficiently reliable" magnitudes (see below), *i.e.* their magnitudes are less than 0.07 ppm. In Table 3 we put two question-marks near such parameters.

High-frequency spectra of some "medium-chain" ethyl acetales of the linear aldehydes **38** which allowed to calculate and ground some "insufficiently reliable" values of the parameters $\Delta\delta^H_2$ and $\Delta\delta^H_{n\text{-}1}$ of the mentioned acetales (and possibly, parameters $\Delta\delta^H_3$ and $\Delta\delta^H_{n\text{-}2}$ for alkanes **1**) are examined below. Since both increments are obtained by calculations and have the absolute value less

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[4] The absorption of every middle methylene group may look as a quintet signal due to the splitting on 4 protons of two neighboring methylene groups. Coupling constants (*J*) of such multiplets have a value of approximately 7 Hz. The distance between extreme maxima of quintet signal may be estimated as the value of about 30 Hz (4 x 7 Hz) corresponding to the value of 0.10 ppm using the instrument with 300 MHz frequency and 0.07 ppm (at the frequency of 400 MHz). The distance between extreme and central peaks must be twice less, *i.e.* 0.04-0.05 ppm.

If the centers of quintet signals of all *t* middle protons coincide with each other and have values of 1.27 ppm, their total signal would be a quintet with the intensity of *t* x 2H. In the reality the centers are shifted and overlaid resulting in "methylene hump" appearance. The hump width is stipulated by two factors: i) instrument frequency; ii) degree of "non-coincidence" of quintet centers of methylene groups of all types (*t*, *r* and *s*). For example, let us examine the quintet signals of two methylene groups minimum distant (by 0.01 ppm) by different sides from the middle of "methylene hump". If the values of centers equal to 1.26 and 1.28 ppm the signal width will increases by 0.02 ppm (by 0.01 ppm in every side) but its form will be complicated. The increase of "shift" difference from 1.27 ppm will extend the quintet signal and transform it into a "methylene hump".

[5] Usually in the spectrum obtained at the instrument with the frequency of 400 MHz it is possible to **clearly determine the whole low-field (right side) quintet signal** nearest to "methylene hump" only in the case when its center signal value is more than 1.37 ppm, *i.e.* exceeds the value of 1.27 ppm by 0.10 ppm what is the equivalent to the inequality $\Delta\delta^H_s \geq 0.10$ ppm. **If the quintet right side combines with "methylene hump", the minimum value of quintet center which may be clearly determined is δ^H_s ~ 1.34 ppm (*i.e.* 1.27 + 0.07).** Hence, the value of $\Delta\delta^H_s$ increment equal to 0.07 ppm seems to be the "minimum reliable" though "approximate" value. Therefore the values of low-field quintet centers selected by us against a background of "methylene hump" within the range of 1.34–1.37 ppm we consider as approximated values. Increments $\Delta\delta^H_r$ and $\Delta\delta^H_s$ of the mentioned signals we marked in the Table 3 by one question-mark.

than 0.07 ppm (the same as other given in Table 3), they are accompanied by two question marks in Table 3.

3.3. Functionalized Compounds of the General Formula I

Long-chain functionalized compounds **I** denoted by bold Arabic numerals (**3-38)** differ from long-chain alkanes **1** (**2**) by the fact that at one (right) end of the molecule they have the functionalized group Y instead of hydrogen atom (*i.e.* Y $\neq$ H and $n = m+1$). In spite of the less quantity of functionalized compounds **I** the literature data about basic spectral parameters d^H_i and d^C_i compared with those for alkanes **1** which are given in [2, 3], we examined and analyzed NMR ^{1}H and ^{13}C spectra of approximately 40 types of the compounds embracing main classes (to our mind) of the aliphatic compounds. The class of ethyl acetales of the linear aldehydes **38** includes only spectral parameters $d^{H,\mathbf{38}}$ due to insufficient literature data about basic spectral parameters $d^{C,\mathbf{38}}$.

All compounds **1-38** with different functional groups (including alkanes **1**, when Y = H) are divided into two groups depending on the nature of that substituent atom attached to the alkyl chain $CH_3(CH_2)_m$–. The first group denoted as "A" involves compounds with the carbon atom attached to the alkyl chain (and it simultaneously belongs to the functional group Y). However we did not examine chemical shifts of such carbon atoms. In the compounds of "B" group the heteroatom Z (including hydrogen atom in alkanes **1**) is attached to the alkyl chain $CH_3(CH_2)_m$–.

The same as for long-chain alkanes **1**(**2**) we founded that the values of the corresponded parameters δ^H_r, δ^C_r, δ^H_s and δ^C_s are constant in spectra NMR ^{1}H and ^{13}C of all types of functionalized long-chain compounds **3-38** within the limits of accepted accuracy. It means that inside every homologous row of the compounds with the same substituent Y but with different value of *m* the increments – parameters $\Delta\delta^H_r$ ($\Delta\delta^C_r$) and $\Delta\delta^H_s$ ($\Delta\delta^C_s$) – are practically the same. Therefore it is advisable to determine their average values closely approximated the boundary values inside the row. The parameters δ^H_r (δ^C_r) and $\Delta\delta^H_r$ ($\Delta\delta^C_r$) of the molecule **I** "methyl" end for all types of the functionalized compounds **3-38** are equal to the analogous parameters for alkanes **1** (**2**) within the range of accepted accuracy (0.02 ppm for NMR ^{1}H and 0.05 ppm for NMR ^{13}C spectra).

As the parameters δ^C_r and $\Delta\delta^C_r$ were given in Table 1, therefore Table 2 represents only averaged increments $\Delta\delta^C_s$ calculated by formula (5):

$$\Delta\delta^C_s = \delta^C_s - \delta^C_t \tag{5}$$

The compounds of "A" group are given in the table at first, and then compounds of "B" group (including repeated data for alkanes **1**). In contrast to alkanes **1** (where number $r = s = 5$ is constant) the number of carbon atoms *s* near the functional group Y in the functionalized compounds **3-37** (where their $\Delta\delta^C_s$ absolute values are equal or more than 0.05 ppm) is different (from 4 to 9). The number of atoms *s* depends upon the nature of substituent Y. The greatest amount ($s = 9$) was found in alkyliodides (**37**).

Table 3 represents averaged values of increments $\Delta\delta^H_r$ and $\Delta\delta^H_s$ calculated for alkanes **1** by formula (6) and for the functionalized compounds **I** by formula (7).

$$\Delta\delta^H_r = \delta^H_r - \delta^H_t = \Delta\delta^{H,\mathbf{1}}_s = \delta^{H,\mathbf{1}}_s - \delta^C_t \tag{6}$$

$$\Delta\delta^H_s = \delta^H_s - \delta^H_t \tag{7}$$

As in Table 2 at first the compounds of "A" group and then the compounds of "B" group are examined in Table 3. As it was mentioned above, the increments with absolute value within 0.07-0.10 ppm are accompanied by one question mark. If the value is less than 0.07 ppm or equal to 0.06 ppm, it is accompanied by two question marks.

In the functionalized compounds **3-38** (the same as for alkanes **1**) the amount of carbon atoms *s* with the increments absolute values $\Delta\delta^H_s \geq 0.07$ ppm (located near "functionalized" end of the molecule) is approximately half of the amount of methylene groups *s* in NMR ^{13}C spectra. The amount of atoms *s* also depends upon the substituent Y nature and for NMR ^{1}H spectra it does not exceed 5 (*i.e.* $s \leq 5$). As it was mentioned above, in all compounds **1-38** the increment $\Delta\delta^H_1$ of the methyl end-group is the only one "reliably determined" **parameter *r*, *i.e.*** its absolute value $\geq$ 0.10 ppm. If two "insufficiently reliable" parameters $\Delta\delta^H_2$ and $\Delta\delta^H_3$ are attached to the mentioned increment $\Delta\delta^H_1$, then the general amount of *r* parameters will be 3. The maximum amount (5) of **parameters *s*** was observed in benzoates (**29**) while for NMR ^{13}C spectra it was 9 in iodoalkanes (**37**).

All averaged values of the increments $\Delta\delta^H_s$ ($\Delta\delta^H_r = \Delta\delta^{H,\mathbf{1}}_s$ for **1**) are given in Table 3. They were calculated from literature data [2, 3] of the basic spectral parameters δ^H_s (their data are absent in Table 3) for long-chain compounds of the general formula **I (1-38).**

Given in Tables 1-3 increments $\Delta\delta^H_s$ and $\Delta\delta^C_s$ are averaged, *i.e.* have approximate values and by our estimation may vary within the limits of $\pm$ 0.01 ppm for NMR ^{1}H and $\pm$ 0.05 ppm for NMR ^{13}C spectra. The calculation procedure is described below for NMR ^{13}C spectra taling iodoalkanes **37** as an example.

The calculation was carried out separately for every 36 types of functionalized compounds **3-38** given in Table 2. At first we calculated increment $\Delta\delta^C_s$ by formula (5) for every *s* atoms of every long-chain homologous compounds of one row. Especially we took into consideration those compounds, data of which concerning "high-frequency" values δ^C_i were available in the sources [2, 3]. For long-chain iodoalkanes **37** there are 3 compounds (starting from 1-iodohexadecane). As a rule, we obtained 2-3 various values for every *s* increments differed by 0.05 ppm (the accepted error). For example, for the increment of C-2 atom we obtained the following $\Delta\delta^C_2$ values, rounded to 0.05 ppm: $\Delta\delta^{H,\mathbf{37}[2]}_2$ = +3.95 ppm (from the spectrum of 1-iodohexadecane obtained by means of the instrument with the frequency of 22.5 MHz and given in [2]); $\Delta\delta^{H,\mathbf{37}[2]}_2$ = +3.90 ppm (1-iodoctadecane, 25 MHz [2]) and $\Delta\delta^{H,\mathbf{37}[3]}_2$ = +3.85 ppm (1-iodododecane, 75 MHz, [3]).

Table 2

Average values of compounds 1 – 37 $\Delta\delta^C_s$ increments (ppm)

Number of comp.	Value of Y in formula I	*s*	$\Delta\delta^C_s$ at *s* equal to								
			9	8	7	6	5	4	3	2	1
2	CH_3	4						-0.05	-0.30	+2.25	-7.00
3	$(CH_3)_2CH$-	4						+0.05	+0.35	-2.20	+9.45
4	$(CH_3)_3C$-	4						+0.10	+1.00	-5.10	+14.70
5	$-CH=CH_2$	5					-0.05	-0.15	-0.50	-0.70	+4.15
6	$-C\equiv CH$	7			-0.05	-0.10	-0.15	-0.55	-0.90	-1.15	-11.30
7	$-C_6H_5$	6				-0.05	-0.10	-0.15	-0.35	+1.80	+6.30
8	$-C\equiv N$	7			-0.10	-0.20	-0.40	-0.95	-1.05	-4.30	-12.65
9	-CH=O	7			-0.05	-0.10	-0.20	-0.35	-0.50	-7.60	+14.20
10	$-C(CH_3)=O$	7			-0.05	-0.10	-0.20	-0.25	-0.50	-5.80	+14.10
11	-C(C6H5)=O	7			-0.05	-0.10	-0.20	-0.25	-0.35	-5.30	+8.90
12[6]	$-C(NH_2)=O$	5			?	?	-0.20	-0.35	-0.45	-4.10	+6.25
13	-C(OH)=O	7			-0.05	-0.10	-0.25	-0.45	-0.65	-5.05	+4.35
14	$-C(OCH_3)=O$	7			-0.05	-0.10	-0.20	-0.40	-0.50	-4.70	+4.40
15	$-C(OC_2H_5)=O$	7			-0.05	-0.10	-0.20	-0.40	-0.50	-4.70	+4.65
16	-C(Cl)=O	7			-0.05	-0.15	-0.35	-0.65	-1.25	-4.65	+17.40
1	H	5					-0.05	-0.30	+2.25	-7.00	-15.65
17	$-NH_2$	4						-0.15	-2.75	+4.25	+12.60
18	-NHR in R-NHR	4						-0.05	-2.20	+0.60	+20.50
19	$-NH(CH_3)$	4						-0.05	-2.25	+0.25	+22.55
20	$-N(CH_3)_2$	4						-0.05	-1.90	-2.15	+30.30
21	**$-NR_2$** in **$R-NR_2$**	4						-0.05	-2.00	-2.60	+24.60
22	**$-NR(CH_3)$** in **$R-NR(CH_3)$**	4						-0.05	-2.05	-2.25	+28.25
23[6]	$-NO_2$	6		?	?	-0.20	-0.40	-0.95	-2.00	-3.75	+46.05
24	-OH	5					-0.05	-0.25	-3.95	+3.10	+33.25
25	-OR in R-OR	5					-0.05	-0.20	-3.45	+0.15	+41.25
26	-OCHO	7			-0.05	-0.15	-0.20	-0.45	-3.85	-1.15	+34.35
27	$-OC(O)CH_3$	5					-0.20	-0.45	-3.80	-1.05	+34.90
28	$-OC(O)C_3H_7$	8		-0.05	-0.10	-0.15	-0.20	-0.45	-3.80	-1.05	+34.65
29	$-OC(O)C_6H_5$	7			-0.05	-0.15	-0.20	-0.40	-3.65	-0.95	+35.35
30	$-OC(O)C(O)C_6H_5$	8		-0.05	-0.10	-0.20	-0.25	-0.50	-3.85	-1.10	+36.25
31	$-OSO_2-C_6H_4-CH_3$-*p*	8		-0.05	-0.15	-0.30	-0.40	-0.90	-4.40	-0.90	+40.95
32	-SH	7			-0.05	-0.10	-0.15	-0.60	-1.30	+4.40	-5.10
33	-SR in R-SR	7			-0.05	-0.10	-0.15	-0.40	-0.70	+0.10	+2.55
34	-F	5					-0.05	-0.35	-4.50	+0.85	+54.45
35	-Cl	7			-0.05	-0.15	-0.25	-0.80	-2.75	+3.00	+15.35
36	-Br	8		-0.05	-0.10	-0.15	-0.25	-0.90	-1.50	+3.15	+4.15
37	-I	9	-0.05	-0.05	-0.10	-0.20	-0.30	-1.20	+0.80	+3.90	-22.60

[6] Through the lack of available examples of amides **12** and nitroalkanes **23** we were not able to determine some values $\Delta\delta^C_6$, $\Delta\delta^C_7$ and $\Delta\delta^C_8$.

Table 3

Averaged values of δ^H_s increments calculated for the compounds 1-38 (ppm)

Compounds number	Y value in the formula **I**	***s*** value	Increment $\Delta\delta^H_s$ at s value equals to:				
			5	4	3	2	1
2	CH_3	2				-0.01??	+0.03??
3	$(CH_3)_2CH$-	1					-0.11
4	$(CH_3)_3C$-	2				-0.02??	-0.11
5	-CH=CH_2	2				+0.10	+0.77
6	-C≡CH	3			+0.12	+0.26	+0.91
7	-C_6H_5	2				+0.33	+1.32
8	-CΞN	3			+0.17	+0.38	+1.06
9	-CH=O	2				+0.36	+1.15
10	-C(CH_3)=O	2				+0.30	+1.14
11	-C(C6H5)=O	4		+0.06??	+0.09	+0.46	+1.68
12	-C(NH_2)=O	3			+0.06??	+0.35	+0.94
13	-C(OH)=O	3			+0.07?	+0.36	+1.08
14	-C(OCH_3)=O	2				+0.35	+1.03
15	-C(OC_2H_5)=O	2				+0.35	+1.01
16	-C(Cl)=O	3			+0.07?	+0.45	+1.61
1	H	3			-0.01??	+0.03??	-0.39
17	-NH_2	2				+0.16	+1.41
18	-NHR in R-NHR	2				+0.21	+1.32
19	-NH(CH_3)	2				+0.21	+1.29
20	-N$(CH_3)_2$	2				+0.18	+0.96
21	-NR_2 in R-NR_2	2				+0.15	+1.11
22	-NR(CH_3) in R-NR(CH_3)	2				+0.18	+1.03
23	-NO_2	3			+0.12	+0.74	+3.11
24	-OH	3			+0.07?	+0.29	+2.35
25	-OR in R-OR	3			+0.08?	+0.29	+2.12
27	-OC(O)CH_3	3			+0.07?	+0.35	+2.78
29	-OC(O)C_6H_5	5	0.04??	0.08?	+0.17	+0.49	+3.04
32	-SH	3			+0.10	+0.34	+1.25
33	-SR in R-SR	3			+0.11	+0.31	+1.22
34	-F	4		+0.07?	+0.12	+0.42	+3.16
35	-Cl	3			+0.15	+0.50	+2.25
36	-Br	3			+0.15	+0.58	+2.13
37	-I	3			+0.11	+0.55	+1.92
38	-CH$(OC_2H_5)_2$	3			+0.05??	+0.09?	+0.33

Then the optimum value of $\Delta\delta^C_s$ increment was determined. For this purpose every 2-3 values of the same increment were substituted in the formulae (9) and (11) (see below) to "check" the calculation of all basic spectral parameters δ^C_i. The calculations were done for all "medium-chain" compounds, the hydrocarbon chain of which consists of 5 or more C atoms. The number of "medium-chain" compounds depends upon the maximum value of *s* (given in Table 2) and it is determined by the nature of substituent Y. For iodoalkanes **37** the number of "medium-chain" compounds is 9: from $C_5H_{11}I$ to $C_{13}H_{25}I$. While comparing the calculated δ^C_i values with experimental ones we chose the value of $\Delta\delta^C_s$ increment ensuring the best coincidence with the experimental results for all compounds which participate in the "checking" calculations. This value is presented in Table 2 as $\Delta\delta^C_s$ value. For example, for the increment of C-2 atom of iodoalkanes **37** three sets of possible values were checked (+3.95, +3.90 and +3.85 ppm) for every 9 examples of medium-chain compounds. The best coincidence was found for $\Delta\delta^C_2$ = 3.90 ppm. It is given in Table 2.

As for NMR ^{13}C spectra, for NMR ^{1}H spectra as a rule, for every *s* increments (for instance, *s* = 3 for iodoalkanes **37**) we also obtained 2-3 values differed by 0.01–0.02 ppm (*i.e*. the difference does not exceed the accepted measurement error). For increment of the long-chain iodoalkanes **37** for two methylene atoms H-1 (*s* =1) we obtained next values: $\Delta\delta^{H,\mathbf{37}}_1$ = +1.92 ppm (from 1-iodononane spectrum, given in [3]) and $\Delta\delta^{H,\mathbf{37}}_1$ = = +1.91 ppm for other compounds.

After "checking" calculations of the spectral parameters δ^H_i for several "medium-chain" compounds in the second stage we chose the optimum value of $\Delta\delta^H{}_s$ increment ensuring the best coincidence with experimental results for all "medium-chain" compounds taking part in "checking" calculations. This optimum value was introduced in Table 3 as an averaged value of $\Delta\delta^H{}_s$ increment (in our example it is $\Delta\delta^{H,\mathbf{37}}{}_1 = +1.91$ ppm).

It should be noted that all $\Delta\delta^H{}_s$ increments with absolute values equal or less than 0.10 ppm and denoted by one or two question marks in Table 3 were received just as the result of checking and refinement of basic spectral parameters $\delta^H{}_i$ for "medium-chain" compounds. All this applies to all $\Delta\delta^C{}_s$ increments which have absolute values equal to 0.05 ppm.

3.4. Peculiarities of Basic Spectral Parameters $\delta^H{}_i$ and $\delta^C{}_i$ for "Medium-Chain" and "Short-Chain" Compounds I

Unlike long-chain compounds, we call the compounds with the amount of carbon atoms in the chain $m < r+s$ as "medium-chain" (and "short-chain") compounds of the general formula **I (1-38)** thereof the middle methylene groups are absent in the molecules[7]. It also means that a part of methylene groups in "medium-chain" compounds and all methylene groups in "short-chain" compounds undergo the simultaneous disturbances from both ends of $-(CH_2)_m-$ fragment. In other words, they include the disturbances occuring due to the exchange of $-(CH_2)_k-$ fragments for hydrogen atom on the left (methyl) end of $-(CH_2)_n-$ fragment remained in the molecule **I**; and $-(CH_2)_l-$ fragment for the functional group Y on the right of it. Carbon and hydrogen atoms in such methylene groups are denoted as "*w*".

We assume that "total disturbance" of the basic spectral parameters $\delta^H{}_w$ of such hydrogen atoms *w* (denoted as the increment $\Delta\delta^H{}_w$) is a function of every increments $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ at the same time. We also assume that the effect of one increment ($\Delta\delta^H{}_r$) on the chemical shift $\delta^H{}_w$ is independent of the effect of other increment ($\Delta\delta^H{}_s$). All this applies to all carbon atoms *w*. Then the total effect (*i.e.* increments $\Delta\delta^H{}_w$ and $\Delta\delta^C{}_w$) will be equal to the sum of both abovementioned increments (Eqs. (8) and (9)):

$$\Delta\delta^H{}_w = \delta^H{}_w - \delta^H{}_t = \Delta\delta^H{}_r + \Delta\delta^H{}_s \quad (8)$$

$$\Delta\delta^C{}_w = \delta^C{}_w - \delta^C{}_t = \Delta\delta^C{}_r + \Delta\delta^C{}_s \quad (9)$$

By using increments $\Delta\delta^H{}_r$, $\Delta\delta^C{}_r$, $\Delta\delta^H{}_s$ and $\Delta\delta^C{}_s$ which are given in Tables 1-3, as well as formulae (10) and (11) derived from the formulae (8) and (9), respectively, we can calculate **all** values of every basic spectral parameters $\delta^H{}_w$ and $\delta^C{}_w$ for every medium- and short-chain functionalized compounds **I** containing **all** types of substituents Y (compounds **3-37**).

$$\delta^H{}_w = \delta^H{}_t + \Delta\delta^H{}_r + \Delta\delta^H{}_s \quad (10)$$

$$\delta^C{}_w = \delta^C{}_t + \Delta\delta^C{}_r + \Delta\delta^C{}_s \quad (11)$$

For the majority of medium-chain compounds **I** we receive a very good coincidence between experimental [2, 3] and calculated basic spectral parameters $\delta^H{}_w$ and $\delta^C{}_w$. The calculation of all $\delta^H{}_w$ values for three homologues of acetales **38** using formula 10 is represented in Table 4 as an example. The calculated values are compared with "high-frequency" experimental data given in [2, 3].

For the calculations we used increments $\Delta\delta^H{}_s$ ($\Delta\delta^H{}_r$), given in Table 1 for the compounds **1** and **38**. For the alkanes **1** the corresponding increments are equal to: $\Delta\delta^{H,\mathbf{1}}{}_1 = -0.39$ ppm; $\Delta\delta^{H,\mathbf{1}}{}_2 = +0.03$ ppm; $\Delta\delta^{H,\mathbf{1}}{}_3 = -0.01$ ppm. The same values are used for long-chain acetales **38**, starting from heptanoic (enanthic) aldehyde $C_7H_{14}O$ (n = 5) and higher: $\Delta\delta^{H,\mathbf{1}}{}_1 = \Delta\delta^{H,\mathbf{38}}{}_n = -0.39$ ppm; $\Delta\delta^{H,\mathbf{1}}{}_2 = \Delta\delta^{H,\mathbf{38}}{}_{n\text{-}1} = \Delta\delta^{H,\mathbf{38}}{}_m = +0.03$ ppm; $\Delta\delta^{H,\mathbf{1}}{}_3 = = \Delta\delta^{H,\mathbf{38}}{}_{n\text{-}2} = \Delta\delta^{H,\mathbf{38}}{}_{m\text{-}1} = -0.01$ ppm. For the functionalized (acetal) end of the molecule **38** the used increments are equal to: $\Delta\delta^{H,\mathbf{38}}{}_1 = +0.33$ ppm; $\Delta\delta^{H,\mathbf{38}}{}_2 = +0.09$ ppm; $\Delta\delta^{H,\mathbf{38}}{}_3 = = +0.05$ ppm. All given in Table 4 experimental values of $\delta^{H,\mathbf{38}}{}_i$ are taken from [2], except the values of propionic aldehyde acetal which were taken from [3]. The experimental data are given in bold in the numerator and calculated results are given in the denominator in square brackets.

The similar calculations were also used to ascertain $\delta^C{}_s$ values. As an example we give below the calculation by formula (11) for 8 values of $\delta^C{}_w$ for 1-iodoctane (octyliodide) and compare it with experimental values (see below). It should be noted that the difference between calculated and experimental values of parameter $\delta^C{}_i$ (*i.e.* $\delta^C{}_{i,calc.}$- $\delta^C{}_{i,exp.}$) does not exceed 0.05 ppm by absolute value in any case.

$\delta^C{}_t$		29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	
$\Delta\delta^C{}_r$		-15.65	-7.00	+2.25	-0.30	-0.05				
	H	**– CH_2**	**– CH_2**	**– CH_2**	**– CH_2**	**– CH_2**	**– CH_2**	**– CH_2**	**– CH_2**	**–I**
$\Delta\delta^C{}_s$	-0.05	-0.05	-0.10	-0.20	-0.30	-1.20	+0.80	+3.90	-22.60	
$\delta^C{}_{w,calc}$		14.05	22.65	31.80	29.15	28.50	30.55	33.65	7.15	
$\delta^C{}_{w,exp.}$		**14.07**	**22.63**	**31.77**	**29.10**	**28.53**	**30.54**	**33.61**	**7.15**	
Difference $\delta^C{}_{i,calc.}$-$\delta^C{}_{i,exp.}$		**-0.02**	**+0.02**	**+0.03**	**+0.05**	**-0.03**	**+0.01**	**+0.04**	**0.00**	

In case of medium-chain compounds **1-37** with the chain length no less than 5 carbon atoms (*i.e.* at $n > 5$), the deviation of calculated by formulae (8-11) the values $\delta^C{}_{w,calc}$ from experimental chemical shifts $\delta^C{}_{w,exp.}$ ($\delta^C{}_{i,calc.}$- $\delta^C{}_{i,exp.}$) does not exceed 0.1 ppm in NMR ^{13}C spectra and parameter ($\delta^H{}_{i,calc.}$- $\delta^H{}_{i,exp.}$) not more than 0.02 ppm in NMR ^1H spectra in 95% of the cases. The same calculations for NMR ^{13}C spectra of medium-chain (n = 4–8) alcohols, esters and tosilates were published earlier [6].

[7] The case when $m = r+s$ should be considered as a boundary one between long- and medium-chain compounds.

Table 4

Calculated and experimental basic spectral parameters $\delta^{H,38}_{i}$ for methyl and methylene groups in the linear aldehydes derivatives – ethyl acetales of the general formula $[CH_3–C^{m}H_2–C^{m-1}H_2–…–C^{2}H_2–C^{1}H_2–CH(OEt)_2]$ (38)

Aldehyde from which acetal is obtained	*m*	$\delta^{H,38}_{CH3}$	Basic spectral parameter $\delta^{H,38}_{i}$, ppm							
			$\delta^{H,38}_{8}$	$\delta^{H,38}_{7}$	$\delta^{H,38}_{6}$	$\delta^{H,38}_{5}$	$\delta^{H,38}_{4}$	$\delta^{H,38}_{3}$	$\delta^{H,38}_{2}$	$\delta^{H,38}_{1}$
Ethanal (acetic)	0	**1.301**								
		[1.21]								
Propanal (propionic)	1	**0.92**								**1.63**
		[0.97]								[1.63]
Butanal (butyric)	2	**0.929**							**1.385**	**1.596**
		[0.93]							[1.39]	[1.59]
Pentanal (valeric)	3	**0.905**						**1.33**	**1.33**	**1.611**
		[0.88]						[1.35]	[1.35]	[1.60]
Hexanal (caproic)	4	**0.889**					**1.31**	**1.31**	**1.36**	**1.602**
		[0.88]					[1.30]	[1.31]	[1.36]	[1.60]
Heptanal (enanthic)	5	**0.882**				**1.30**	**1.27**	**1.32**	**1.36**	**1.602**
		[0.88]				[1.30]	[1.27]	[1.32]	[1.36]	[1.60]
Decanal	8	**0.879**	**1.32**	**1.27**	**1.27–1.32**				**1.37**	**1.599**
		[0.88]	[1.30]	[1.26]	[1.27]	[1.27]	[1.27]	[1.32]	[1.36]	[1.60]

In the case of "short-chain" compounds **1-38** usually with the chain length of less than 3 atoms ($m \leq 1$ in the formula **I**) the deviation between calculated and experimental chemical shifts δ^{H}_{w} exceeds 0.1 ppm for some types of hydrogen atoms and more than 0.5 ppm of carbon atoms.

And for the compounds **I** with a very short chain (n = 2, m = 1) or even without the chain (n = 1, m = 0; for example it is methyliodide in the case of 1-iodoalkanes **37**) the calculated values δ^{C}_{w} describes only the order of magnitude of experimental chemical shift $\delta^{C}_{w,exp.}$, because their difference is 1–2 ppm. All this applies to parameters $\delta^{H}_{w,exp.}$ for a very short chain compounds **I**. The examples of the mentioned calculations for two lowest homologues of acetales **38** are also represented in Table 4.

The good correlation between calculated and experimental values of δ^{H}_{i} and δ^{C}_{i} parameters allows to predict the values of chemical shifts for those functionalized compounds **I** NMR ^{13}C and NMR ^{1}H spectra of which are not described in the literature.

4. Conclusions

1. We suggested the new method of all spectral changes calculations occurring in NMR ^{1}H and ^{13}C spectra of $CH_3(CH_2)_mY$ (**I**) molecule during the introduction of various substituents Y in the molecule of reference substance – linear alkane. The suggested conception assumed a virtual transformation of the hypothetical alkane molecule $H\text{-}(CH_2)_k–(CH_2)_m–(CH_2)_l–H$ (**II**) with the infinitely long hydrocarbon chain-$(CH_2)_k$– and –$(CH_2)_l$– into the real substance $CH_3(CH_2)_mY$ (**I**). In the first approximation it may be accepted that every "disturbance" occuring at both ends of alkyl chain during the (**II**→**I**) conversion independently affects the protons (δ^{H}_{i}) and carbon (δ^{C}_{i}) chemical shifts of every methylene groups. For the long-chain molecules the methylene groups undergo the effect of one or none "disturbing factor" depending on its position in the chain.

2. For "medium-" and "short-chain" compounds **I** both "disturbing factors" from both ends of alkyl chain influence the proton (δ^{H}_{w}) and carbon (δ^{C}_{w}) values of every w methylene groups. Their total effect is accepted as an additive one.

3. In the compounds **I** with the shortest alkyl chain (less than 3 carbon atoms) the mentioned additive factor takes place, as well as unknown factors that causes the increasing difference between calculated and experimental δ^{H}_{i} and δ^{C}_{i} parameters.

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ОСОБЛИВОСТІ ^{1}Н і ^{13}С ЯМР СПЕКТРІВ АЛКІЛЬНИХ ГРУП У ФУНКЦІОНАЛІЗОВАНИХ ЛІНІЙНИХ АЛКАНАХ ЗАГАЛЬНОЇ ФОРМУЛИ $CH_3(CH_2)_mY$

Анотація. *Розглянуто дані літератури ^{1}H і ^{13}C ЯМР спектрів лінійних алканів X-$(CH_2)_n$-Y (**I**), (де X = H; Y – 38 різних замісників, включаючи H і CH_3). Запропоновано новий універсальний спосіб оцінювання величин хімічних зсувів метиленових груп ($\delta^{H}_{CH2} = \delta^{H}_{i}$, $\delta^{C}_{CH2} = \delta^{C}_{i}$, i = 1–38) у **I**. Концепція методу полягає в зміні значень δ^{H}_{i} і δ^{C}_{i} для кожної метиленової групи в **I** (які, відповідно, називаються інкрементами $\Delta\delta^{H}_{i}$ і $\Delta\delta^{C}_{i}$) в результаті перетворення гіпотетичного алкана $-(CH_2)_K-(CH_2)_n-(CH_2)_{\Gamma}-$ (**II**) внаслідок заміщення безкінечно довгих фрагментів $-(CH_2)_K-$ і $-(CH_2)_{\Gamma}-$ замісниками X та Y. Розраховані інкременти $\Delta\delta^{H}_{i}$ і $\Delta\delta^{C}_{i}$ для всіх типів замісників. Запропонований метод дає можливість розраховувати параметри δ^{H}_{i} і δ^{C}_{i} для неопублікованих ^{1}H і ^{13}C ЯМР спектрів довго- і середньо-ланцюгових сполук **I**. Приведено приклад розрахунків.*

Ключові слова: *^{1}H і ^{13}C ЯМР спектри, l-заміщений лінійний алкан, довго-, середньо- і коротко ланцюгові сполуки, базовий спектральний параметр, інкремент.*