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PECULIARITIES OF NMR ^{1}H 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 spectra of linear alkanes X-$(CH_2)_n$-Y (**I**), (X = H; Y - 38 different substituents, including H and CH_3) were considered. The new universal way to estimate the chemical shifts of the methylene groups ($\delta^H_{CH2} = \delta^H_i$, i = 1 ÷ 36) in **I** was proposed. The concept of it considers changes in the values δ^H_i of each methylene groups in **I** (called as increments $\Delta\delta^H_i$) 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 $\Delta\delta^H_i$ for all substituent types were culculated and tabulated. The example of calculations was given. The proposed method let to compute the δ^H_i parameter for the unpublished NMR ^{1}H spectra of long- and medium-chain compounds **I.**

Keywords: NMR ^{1}H spectra, 1-substituted linear alkanes, long-, medium- and short-chain compounds, basic spectral parameters δ^H_i, increments $\Delta\delta^H_i$ calculated $\delta^H_{i,calc}$ and experimental $\delta^H_{i,exp}$ parameters.

1. Introduction

One of the main important and designing problems of natural philosophy is an interaction between substance structure and its properties. To our mind the final decision for this problem is impossible. As our knowledge about new properties is developed, 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 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, correspondingly) 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 proton chemical shift (δ^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 elaborate. Moreover, some determined correlations had not well-defined theoretical explanations. For example, in ethylhalogenides CH_3–CH_2–Hal the values δ^H_{CH2} of methylene group protons depend in direct proportion to the electronegativity of halogen atom and for the methyl protons δ^H_{CH3} this proportion is inversely.

Since sixties NMR ^{13}C spectra were used in the organic chemistry too. 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.

1.1. The aim of investigation

We decided to bridge this gap and chose a traditional way of decision – from the simple problem to the complex one. Monosubstituted nonbranched alkanes (especially for those cases when the substituent was at the chain beginning) and the simplest aromatic compounds (benzene monosubstituted derivatives) were examined as the simplest compounds. The spectral parameters NMR ^1H and ^{13}C were chosen as investigation objects. The aim was to investigate **all spectral changes occurring in NMR ^1H 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 ^1H 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 ^1H 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. Accordingly to the purpose we selected rows of investigated compounds. If the regular character of the nuclei is observed depending on 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 ^1H 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 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.

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[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.

$$\overset{\delta^{C}_{i}}{CH_3–(CH_2)_m–Y} \leftrightarrow \overset{\delta^{C}_{i}}{H–(CH_2)_n–Y}$$

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**); $O_2S(C_6H_4\text{-}CH_3\text{-}p)$-O- (31); HS- (**32**); RS- (**33**); F- (**34**); Cl- (**35**); Br- (**36**); I- (**37**), $(C_2H_5O)_2CH$- (**38**).

In the accompanying report [2] the regularities of signals behavior of carbon atom nuclei are described in NMR ^{13}C spectra depending on the compound structure inside the rows of simple aliphatic compounds (**I**). This report is the second part of our investigations. It concerning the attempts to determine the main **factors** affecting the chemical shifts values of hydrogen nuclei (δ^{H}_{i}) in NMR ^{1}H spectra of compounds (**I**) in the external contour of alkyl fragment, i.e. total amount of hydrogen atoms bonded with carbon atoms which compose the internal contour. 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 δ^{H}_{i} of those hydrogen atoms which form the external counter of alkyl fragment of molecule $CH_3(CH_2)_m$-Y and location of these atoms in the chain.

1.2. Investigation procedure

There are a lot of empirical correlations to calculate the δ^{H}_{i} parameters in the linear alkanes. We don't 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 δ^{H}_{i} (i = 1– n) for all hydrogen atoms of $n = m + 1$ 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 hydrocarbon 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 hydrogen atoms 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 $\delta^H{}_i$, denoted as $\delta^H{}_{hyp.}$

$$\overset{\delta^c_k}{-\!\!(CH_2)_k\!\!-}\overset{\delta^c_n}{(CH_2)_n\!\!-}\overset{\delta^c_l}{(CH_2)_l\!\!-}$$

II

$$k = l = \infty$$

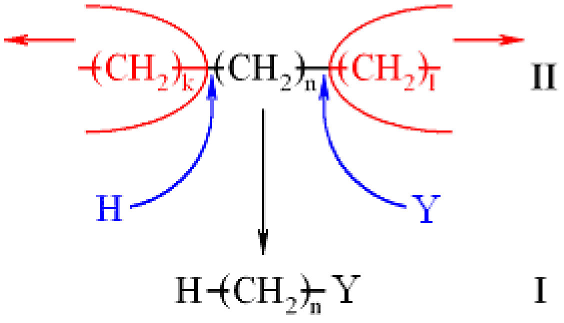
$$\delta^c_k = \delta^c_l = \delta^c_n = \delta^c_{hyp.}$$

The same as earlier [2] we used the transformation of hypothetic linear alkane (**II**) with extremely long carbon chain of the general $H\text{-}(CH_2)_k\text{-}(CH_2)_n\text{-}(CH_2)_l\text{-}H$ into a real molecule of the investigated compound **I**. We assumed that coefficients *k* and *l* are infinitely large in the compound **II** and the coefficient *m* is a finite quantity equal to the coefficient *m* in the formula **I**.

The hypothetic transformation ([2], Fig. 1) of the virtual molecule **II** into the real molecule **I** consists of the flowing stages: 1) at the left end of the molecule **II** the infinitely long methylene fragment $–(CH_2)_k–$ is exchanged for hydrogen atom; 2) at the right end of the chain the fragment $–(CH_2)_l–$ is exchanged for the functional group Y.

Fig. 1

The hypothetic transformation of virtual alkane II to the investigated compounds I



2. Experimental part

The same as for NMR ^{13}C spectra [2] we used literature data about basic spectral parameters $\delta^H{}_i$ to study the spectra peculiarities of hydrogen atoms nuclei composing the external contour of the molecules **I**. The choice of literature sources was grounded on the observation of their reliability and compatibility, criteria of which are discussed in [3]. We used $\delta^H{}_i$ values obtained in deuterochloroform as a solvent and presented in the reference book [4, 5]. Spectra obtained in other solvent, e.g. DMSO-d6, we do not examine here. The parameters $\delta^H{}_i{}^{[4]}$, given in [4] were obtained using instruments with different frequency: low-frequency (90 MHz) and high-frequency (300 or 400 MHz). In those cases when both values $\delta^H{}_i$ 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.

The authors of data represented in [4] give their own attribution of spectra signals to the absorption of definite types of hydrogen atom nuclei and we agree with them in the most cases. Sometimes we present our own attribution of signals (more correct, to our mind). The authors of data represented in [5] do not give their own attribution of spectra signals; therefore we do this by ourselves. We estimate the inaccuracy of measurements as ± 0.02 ppm. Henceforth all values of $\delta^{H}{}_{i}$ parameters are rounded to the nearest number divisible by 0.01 ppm. Sometimes authors [4] present the results with the accuracy of 0.001 ppm.

3. Results and Discussion

3.1. Compounds of the general formula (I) with long alkyl chain ("long-chain" compounds I)

We assume that all 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 $\delta^{H}{}_{i}$ denoted as $\delta^{H}{}_{hyp}$. Obviously that due to the transformation of the hypothetic alkane **II** to the real compound **I** the value $\delta^{H}{}_{i}$ of all (or some) hydrogen atoms is changed in $–(CH_2)_m–$ fragment. These changes are mainly applied to r hydrogen atoms in $(CH_2)_n$ fragment which are closer to the place where $H(CH_2)_k$ fragment is exchanged for the hydrogen atom (so called "methyl" end of the fragment). The same changes will be for s carbon atoms of "functionalized" end of $(CH_2)_n$ fragment.

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 (Fig. 4). For these compounds the inequality (1) must take place:

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

The "additional" methylene groups in amount of "t", which do not belong to the 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 $\delta^{H}{}_{i}$ of hydrogen atoms t of "middle" methylene groups in alkyl chains are denoted as $\delta^{H}{}_{t}$. We assume the value of the mentioned parameter is equal to the virtual parameter $\delta^{H}{}_{hyp}$, i.e. $\delta^{H}{}_{hyp.} = \delta^{H}{}_{t}$. Parameters $\delta^{H}{}_{i}$ of hydrogen atom nuclei of the "end" fragments $(CH_2)_r$ and $(CH_2)_s$ of the molecule **I** we denote as $\delta^{H}{}_{r}$ and $\delta^{H}{}_{s}$.

$$\delta^{H}{}_{r} \qquad \delta^{H}{}_{t} \qquad \delta^{H}{}_{s}$$

$$H\text{-}(CH_2)_r–(CH_2)_t–(CH_2)_s–Y$$

$$\mathbf{I}, \qquad n = r + s + t$$

"Long-chain" molecules **I**

The differences between parameters of “end” methylene groups ($\delta^H{}_r$ and $\delta^H{}_s$) and middle methylene groups $\delta^H{}_t$ are caused by “molecule disturbance” taking place 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 $\Delta\delta^H{}_s$ and equal to the difference between real (experimental) values of the basic parameter $\delta^H{}_i$ in the fragment $(CH_2)_m$ of the molecule **I** and constant value $\delta^H{}_t$. Increments $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ are calculated by the formulas (2) and (3):

$$\Delta\delta^H{}_r = \delta^H{}_r - \delta^H{}_{hyp} \qquad (2)$$

$$\Delta\delta^H{}_s = \delta^H{}_s - \delta^H{}_{hyp} \qquad (3)$$

Obviously, the farther carbon atom (*i*) is situated in alkyl chain from the “disturbance point”, the absolute value of increments $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ will be less and vice versa.

3.2. Linear alkanes of the general formula 2 (Y = CH_3 in the formula I)

We assumed in [2] that linear alkanes with chain length no less than 11 carbon atoms are the most similar compounds modeling spectral properties of the hypothetic alkane **II**. All 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. 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. 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* varies 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 those determined before [2] 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 NMR ^{1}H spectra of esters [6] 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 determined is confirmed (see below).

It is advisable to examine in long-chain alkalnes **1** the spectral parameters $\delta^H{}_i$ and $\Delta\delta^H{}_i$ for six hydrogen atoms of two methyl end-groups C^1 and C^n. These groups are not methylene groups of $–(CH_2)_m–$ fragment but imprescriptibly belong to the alkyl chain.

Since the values $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ are measure of changes (molecule disturbance) while conversion of hypothetical structure **II** to the real molecules **I**, numerical values of $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ are equal by pairs (i.e. $\delta^H{}_1 = \delta^H{}_n$, $\delta^H{}_2 = \delta^H{}_{n-1}$, etc.) in the spectra of long-chain alkalnes **1** (Y=H) due to the molecule symmetry. Hence, corresponding increments are equal as well, i.e. $\Delta\delta^H{}_r = \Delta\delta^H{}_s$. Their absolute values decrease as they approach to the middle of the chain.

In NMR^{1}H spectra given in [3, 4] for the long-chain linear alkanes **1** starting from C_6H_{14} to $C_{38}H_{78}$ the absorption of middle methylene groups is shown as expanded singlet signal (so called "methylene hump"). The value of its center may be accepted as 1.27±0.02 ppm within the error range[2]. Increments **$\Delta\delta^H_r$ and $\Delta\delta^H_s$, exceeding the value of 0.07 ppm** by absolute value[3], 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 the Table 1 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 grounded some "insufficiently reliable" values of the parameters $\Delta\delta^H_2$ and $\Delta\delta^H_{n-1}$ of the mentioned acetales (and possibly, parameters $\Delta\delta^H_3$ and $\Delta\delta^H_{n-2}$) for alkanes **1** are examined below. Since both increments are obtained by calculations and have the absolute value less than 0.07 ppm (the same as other given in the Table), they are accompanied by two question marks in the Table 1.

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 the one end of the molecule they have functionalized group Y instead of hydrogen atom (*i.e.* Y ≠ H and $n = m$+1). We analyzed NMR ^{1}H spectra of approximately 40 types of the compounds embracing main classes of the aliphatic compounds. The same numeration of the compounds **I** as for NMR ^{13}C spectra [2] was accepted. Additionally we introduced the class of ethyl acetales of the linear aldehydes **38**.

The same as in [2] all compounds **1-38** 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

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[2] 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 has 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 *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; 2) degree of "non-coincidence" of quintet centers of methylene groups all types (*t, r* and *s*). For example, let's 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 signal and transform it into "methylene hump".

[3] Usually in the spectrum obtained at the instrument with the frequency of 400 MHz it is possible to **clearly** determine the quintet signal nearest to "methylene hump" only in the case when its center signal is less 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 is $\delta^H_s \sim 1.34$ 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 by question-mark.

"A" involves compounds with the carbon atom attached to the alkyl chain. In the compounds of "B" group the heteroatom Z is attached to the alkyl chain $CH_3(CH_2)_m$–.

The same as for NMR ^{13}C spectra [2], the constancy of the parameters $\delta^H{}_r$ and $\delta^H{}_s$ was observed in all NMR ^1H spectra of the long-chain compounds **1-38** within the range of accepted measurement accuracy. It means that inside every homologous row of the compounds with the same substituent Y but with different value of *m* the parameters $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ are practically the same. Therefore it is advisable to determine their average values closely approximated the boundary values inside the row. The parameters $\delta^H{}_r$ and $\Delta\delta^H{}_r$ 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). Table 1 represents averaged values of increments $\Delta\delta^H{}_r$ and $\Delta\delta^H{}_s$ calculated for alkanes **1** by formula (4) and for the functionalized compounds **I** by formula (5).

$$\Delta\delta^H{}_r = \delta^H{}_r - \delta^H{}_t \tag{4}$$

$$\Delta\delta^H{}_s = \delta^H{}_s - \delta^H{}_t \tag{5}$$

In Table 1 the compounds of "A" group are examined at first and then the compounds of "B" group. 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 [2]. The amount of atoms *s* depends upon the substituent Y nature and for NMR ^1H spectra it does not exceed 5 (i.e. s ≥ 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 ≥ 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 will be 3. The maximum amount (5) of **parameters *s*** was observed in oxybenzoates (**29**) while for NMR ^{13}C spectra [2] it was 9 in iodoalkanes (**37**).

All averaged values of the increments $\Delta\delta^H{}_s$ ($\Delta\delta^H{}_r$) are given in Table 1. They were calculated from literature data [4, 5] of the basic spectral parameters $\delta^H{}_s$ (their data are absent in the Table 1) for long-chain compounds of the general formula **I (1-38).**

Table 1

Averaged values of $\delta^H{}_s$ increments calculated for the compounds 1-38

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	-CΞCH	3			+0.12	+0.26	+0.91
7	-C$_6$H$_5$	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$_2$H$_5$)=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$_3$) в 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$_6$H$_5$	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

As it was mentioned above, the increments $\Delta\delta^{H}_{s}$ are averaged values; therefore they have approximate values varied within ± 0.01 ppm. The calculation procedure is described below taling iodoalkanes **37** as an example. The procedure is the same as that in [2] for NMR ^{13}C spectra.

The calculation was carried out separately for every 36 types of functionalized compounds **3-38** given in Table 1. At first we calculated increment $\Delta\delta^{H}_{s}$ by formula (5) for every *s* atoms of every long-chain homologous compounds of one row. We took those compounds, data of which concerning “high-frequency” values δ^{H}_{i} were available in the sources [4, 5]. For example, for long-chain iodoalkanes**37** there are 6 compounds (starting from iodoctane). As a rule, for every *s* increments (*s* = 3) we obtained 2-3 values differed by 0.01-0.02 ppm (i.e. the difference does not exceed the accepted measurement error). For instance, for the increment of two methylene atoms H-1 (*s* =1) we obtained: $\Delta\delta^{H,\mathbf{37}}_{1}$ = +1.92 ppm (from 1-iodononane spectrum, given in [5]) and $\Delta\delta^{H,\mathbf{37}}_{1}$ = +1.91 ppm for other compounds.

After “checking” calculations (see [2]) of the spectral parameters δ^{H}_{i} for several “medium-chain” compounds 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 entered in the Table 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 question marks in Table 1 were entered just as a result of checking and refinement of basic spectral parameters δ^{H}_{i} for “medium-chain” compounds.

3.4. Peculiarities of basic spectral parameters δ^{H}_{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 absence in the molecules[4]. It also means that a part of carbon atoms in “medium-chain” compounds and all carbon atoms in “short-chain” compounds undergo the simultaneous disturbances from both ends of $–(CH_2)_m–$ fragment. In other words, the disturbances occur due to the exchange of $–(CH_2)_k–$ fragments for hydrogen atom on the left of –

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

$(CH_2)_n-$ fragment remained in the molecule **I**; and $-(CH_2)_l-$ fragment for the functional group Y on the right of it. Such carbon atoms are denoted as "*w*".

We assume that "total disturbance" of the basic spectral parameters δ^H_w of such 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 δ^H_w is independent of the effect of other increment ($\Delta\delta^H_s$). Then the total effect (i.e. increment $\Delta\delta^H_w$) will be equal to the sum of both increments (Equation 6):

$$\Delta\delta^H_w = \delta^H_w - \delta^H_t = \Delta\delta^H_r + \Delta\delta^H_s \qquad (6)$$

Calculated values of basic spectral parameters δ^H_w used for the checking (see above) of every "medium-" and "short-chain" compounds **I** with any Y substituent (compounds **1-38**) may be calculated by the formula (7) derived from the formula (6):

$$\delta^H_w = \delta^H_t + \Delta\delta^H_r + \Delta\delta^H_s \qquad (7)$$

For the majority of medium-chain compounds **I** there is a good coincidence between experimental [4, 5] and calculated basic spectral parameters δ^H_w. The calculation of all δ^H_w values for three homologues of acetales **38** is represented in Table 2 as an example. The calculated values are compared with "high-frequency" experimental data given in [4, 5]. In the case of "short-chain" compounds **1-38** 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. The examples of mentioned calculations for two lowest homologues of acetales **38** are also represented in Table 2.

Table 2

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 $[CH_3\text{-}C^mH_2\text{-}C^{m-1}H_2\text{-}\ldots\text{-}C^2H_2\text{-}C^1H_2\text{-}CH(OEt)_2]$ (38)

No.	Aldehyde from which acetal is	*m*	$\delta^{H,38}_{CH3}$	Basic spectral parameter $\delta^{H,38}_i$, ppm							
				$\delta^{H,38}_8$	$\delta^{H,38}_7$	$\delta^{H,38}_6$	$\delta^{H,38}_5$	$\delta^{H,38}_4$	$\delta^{H,38}_3$	$\delta^{H,38}_2$	$\delta^{H,38}_1$
1	Ethanal (acetic)	0	**1.301**								
			[1.21]								
2	Propanal (propionic)	1	**0.92**								**1.63**
			[0.97]								[1.63]
3	Butanal (butyric)	2	**0.929**							**1.385**	**1.596**
			[0.93]							[1.39]	[1.59]
4	Pentanal (valeric)	3	**0.905**						**1.33**	**1.33**	**1.611**
			[0.88]						[1.35]	[1.35]	[1.60]
5	Hexanal (caproic)	4	**0.889**					**1.31**	**1.31**	**1.36**	**1.602**
			[0.88]					[1.30]	[1.31]	[1.36]	[1.60]
6	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]
7	Decanal	8	**0.879**	**1.32**	**1.27**	**От 1.27 до 1.32**				**1.37**	**1.599**
			[0.88]	[1.30]	[1.26]	[1.27]	[1.27]	[1.27]	[1.32]	[1.36]	[1.60]

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; $\Delta\delta^{H,\mathbf{1}}_{2} = \Delta\delta^{H,\mathbf{38}}_{n-1} = \Delta\delta^{H,\mathbf{38}}_{m} = +\ 0.03$ ppm; $\Delta\delta^{H,\mathbf{1}}_{3} = \Delta\delta^{H,\mathbf{38}}_{n-2} = \Delta\delta^{H,\mathbf{38}}_{m-1} = -\ 0.01$ 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 2 experimental values of $\delta^{H,\mathbf{38}}_{i}$ are taken from [4], except values of propionic aldehyde acetal which were taken from [5]. The experimental data are given by bold in numerator and calculated results are given in denominator in square brackets.

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

4 Conclusions

1. In the first approximation it may be accepted that every “disturbance” occuring at the both ends of alkyl chain during the conversion of hypothetic molecule **II** to the real molecules **I** affects independently the protons chemical shift δ^{H}_{i} of every methylene groups. For the long-chain molecules the carbon atom undergoes the effect of one or none “disturbing factor” depending on atom position.
2. For “medium-“ and “short-chain” compounds **I** both “disturbing factors” from both ends of alkyl chain influence the proton δ^{H}_{w} values of every w methylene groups. Their total effect is accepted as additive one.
3. In the compounds **I** with the shortest alkyl chain (i.e. at $n \leq 2$) the mentioned additive factor takes place, as well as unknown factors what causes the difference between calculated and experimental δ^{H}_{i} parameters.

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