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PECULIARITIES OF NMR ^{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 ^{13}C spectra of linear alkanes X-(CH2)$_n$-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 ($\delta^C_{CH2} = \delta^C_i$, i = 1 ÷ 36) in **I** was proposed. The concept of it considers changes in the values δ^C_i of each carbon atom in **I** (called as increments $\Delta\delta^C_i$) as a result of conversion to **I** of a hypothetical alkane $-(CH_2)_k-(CH_2)_n-(CH_2)_l-$ (**II**) by replacing infinitely long fragments $-(CH_2)_k-$ and $-(CH_2)_l-$ of it with the substituents X and Y. Increments $\Delta\delta^C_i$ for all substituent types were culculated and tabulated. The example of calculations was given. The proposed method let to compute the δ^C_i parameters for the unpublished NMR ^{13}C spectra of long- and medium-chain compounds **I.**

Keywords: NMR ^{13}C spectra, 1-substituted linear alkanes, long-, medium- and short-chain compounds, basic spectral parameters δ^C_i, increments $\Delta\delta^C_i$, calculated $\delta^C_{i,calc}$ and experimental $\delta^C_{i,exp}$ 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 ^{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. 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 ^{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 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.

$$\delta^C_i \qquad\qquad \delta^C_i$$

$$CH_3{–}(CH_2)_m{–}Y \leftrightarrow H{–}(CH_2)_n{–}Y$$

I, *n = m + **1***

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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.

where Y = H- (**1**); CH_3- (**2**); $(CH_3)_2CH$- (**3**); $(CH_3)_3C$- (**4**); $CH_2{=}CH$- (**5**); $C{\equiv}CH$- (**6**); C_6H_5- (**7**); $N{\equiv}C$- (**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**).

This report is the first part of our investigations concerning the attempts to determine the main **factors** affecting the chemical shifts values of carbon nuclei (δ^C_i) in the internal contour of alkyl fragment in NMR^{13}C spectra of compounds (**I**). 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^C_i of those carbon atoms which form the internal counter of alkyl fragment of molecule $CH_3(CH_2)_m$-Y and location of these atoms in the chain.

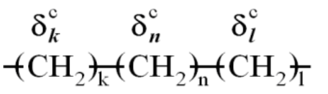
1.2. Investigation procedure

There are a lot of empirical correlations to calculate the δ^C_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^C_i (i = 1– n) for all $n = m + 1$ carbon atoms 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 carbon 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 δ^C_i, denoted as $\delta^C_{hyp.}$



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

II

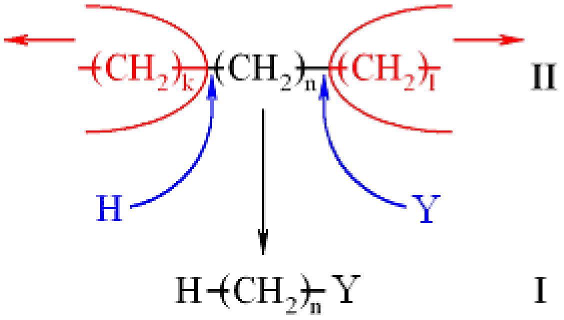
$$k = l = \infty$$

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

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 δ^{C}_{hyp} parameters. The infinitely long methylene fragment $-(CH_2)_k-$ will be changed for the hydrogen atom at the left side of the molecule **II**, and fragment $-(CH_2)_l-$ at 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



2. Experimental

All 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]. To discuss the peculiarities of the basic spectral parameters δ^{C} we took only values obtained during spectrum recording in deuterochloroform as a solvent. 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 (75 MHz). The drawback of 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 at low- and high-frequency instruments for the same signals.

In the spectra given in [1 the author’s attribution of the signals to the absorption of particular nuclei of carbon atoms is stated. In the most cases we agree with the authors, otherwise we suggest our own attribution. 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]. 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.

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

3. Results and Discussion

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

3.1.1. Used symbols

We assume that all carbon atoms of alkyl chain in the hypothetic alkane **II** (including m atoms of methylene groups) are located in the same chemical surrounding and have the same values of the parameter δ^C_i**,** denoted as $\delta^C_{hyp.}$. It is logically to assume that the change of δ^C_i value for all or some of the carbon atoms of alkyl chain should take place in the fragment $(CH_2)_n$ as a result of above-mentioned transfer from hypothetical infinitely long alkane **II** to the real compound **I**. Obviously such changes concern only those *r* hydrocarbon atoms at the left (methyl) end in the linear fragment $(CH_2)_n$ of the molecule **I** which are the closest to the point of $H(CH_2)_k$– substitution for hydrogen atom (*i.e.* to the point of molecule **II** disturbance). We denoted the δ^C_i parameters of *r* methylene groups as δ^C_r. The same situation takes place during the substitution of $H(CH_2)_l$–fragment for Y group at the right (functionalized) end for *s* atoms of $(CH_2)_n$ fragment, for which $\delta^C_i = \delta^C_s$. Hence, in order to avoid the superposition of different "disturbances", the length of $H(CH_2)_k$– chain in the molecule **I** should be not less than total amount of hydrocarbon atoms *r+s*, *i.e.*

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

If the number of hydrocarbon atoms *n* in the compounds **I** exceeds the sum *r+s* at least by one[3] (*i.e.n* > *r+s*+1), we denote them as "long-chain"[4]. Methylene groups in amount of *t* which do not belong to the number *r* and *s* of chain methylene groups were denoted as "middle" groups (so, the inequality (1) is equivalent to the inequality t ≥ 1). The values of basic parameters δ^C_i of carbon atoms t of "middle" methylene groups in alkyl chains are denoted as δ^C_t. Hence, at least one "middle" methylene group (*i.e.* $t \geq 1$) with the parameters $\delta^C_i = \delta^C_t$ must be in the "long-chain" compounds **I**.

$$\delta^C_r \qquad \delta^C_t \qquad \delta^C_s$$

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

I, $n = r + s + t$

"Long-chain" molecules **I**

The differences between parameters of "end" methylene groups (δ^C_r and δ^C_s) and middle methylene groups $\delta^C_t = \delta^C_{hyp.}$ are caused by "molecule disturbance" taking place during the

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[3] The case when $m = r+s$ and $t = 0$ should be considered as boundary one between long- and medium-chain compounds.

[4] The division of linear alkyl groups by chain length was repeatedly useful. Being used here terms "long-, medium and short-chain" alkyl groups do not correspond to the similar terms in the previous works which describe the NMR ^1H spectra of benzoates and benzoylformates. Alkyl groups consisting of 4 atoms (butyl) and more were united into "long-chain"; alkyl groups of 2 (ethyl) and 3 (propyl) hydrocarbons atoms – into "medium-chain" and methyl group – into "short-chain".

transformation from **II** to **I**. The values of the mentioned differences (so called "increments") are determined by differential spectral parameters $\Delta\delta^C_r$, $\Delta\delta^C_s$ and equal to the difference between real (experimental) values of the basic parameter δ^C_i in the fragment $(CH_2)_m$ of the molecule **I** and constant value $\delta^C_t = \delta^C_{hyp.}$. Increments $\Delta\delta^C_r$ and $\Delta\delta^C_s$ are calculated by the formulas (2) and (3):

$$\Delta\delta^C_r = \delta^C_r - \delta^C_{hyp.} \qquad (2)$$

$$\Delta\delta^C_s = \delta^C_s - \delta^C_{hyp.} \qquad (3)$$

Obviously, the farther carbon atom (i) is situated in alkyl chain from the "disturbance point", the absolute value of increments $\Delta\delta^C_r$ and $\Delta\delta^C_s$ will be less and vice versa.

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

The nearest compounds simulated the spectral properties of hypothetical alkane with infinitely long chain **II** are linear alkanes with the chain length more than 11 (see below); 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 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. They contain 2 methyl and *m* methylene groups. So, the ratio between *m* and *n* is *m* = *n*-2. Therefore, the linear alkanes **1** with the chain length of more than 11 hydrogen atoms, *i.e.* starting from undecane (*n* = 11, *m* = 9) and higher are denoted by the general term "long-chain alkanes".

To our mind it is advisable to examine here spectral parameters δ^C_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 are also the part of the alkyl chain in the compounds **1**, though they are not declared above methylene groups of the fragment $-(CH_2)_m-$.

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[5]. 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.* **$\underline{\delta^C_{hyp} = \delta^C_t = 29.75 \text{ ppm.}}$**

Since the values $\Delta\delta^C_r$ and $\Delta\delta^C_s$ are measure of changes of molecule disturbance while conversion of hypothetical structure **II** to the real molecules **I**, numerical values of $\Delta\delta^C_r$ and $\Delta\delta^C_s$ are equal by pairs (i.e. $\delta^C_1 = \delta^C_n$, $\delta^C_2 = \delta^C_{n-1}$, etc.) in the spectra of long-chain alkalnes **1** (Y=H) due to the molecule symmetry. Hence, in **1** corresponding increments are equal as well, i.e. $\Delta\delta^C_r = \Delta\delta^C_s$.

We found that (as we expect) the 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 δ^C_t = 29.75 ppm equal to 0.05 ppm by absolute value. Therefore, according to

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

inequality (1) we determined linear alkanes starting from undecane $C_{11}H_{24}$ as long-chain alkanes because 11=5+5+1.

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.*: $\delta^C_1 = \delta^C_n$, $\delta^C_2 = \delta^C_{n-1}$, $\delta^C_3 = \delta^C_{n-2}$, $\delta^C_4 = \delta^C_{n-3}$ and$\delta^C_5 = \delta^C_{n-4}$. The experimental values [2, 3], averaged spectral parameters δ^C_r (δ^C_s) and δ^C_t for long-chain alkanes 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.

$$\Delta\delta^C_r = \Delta\delta^C_s = \delta^C_r - \delta^C_t \qquad (4)$$

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)	**14.10**	**22.75**	**32.00**	**29.45**	**29.70**	**29.75**
Averaged experimental parameterδ^C_tin alkanes**1**, accepted to be equal to the virtual parameter $\delta^C_{hyp.}$ in **II**	29.75	29.75	29.75	29.75	29.75	29.75
Averaged increment $\Delta\delta^C_r$ ($\Delta\delta^C_s$)	**-15.65**	**-7.00**	**+2.25**	**-0.30**	**-0.05**	**0.00**

Here we present averaged values of the basic spectral parametersδ^C_r (δ^C_s) in the long-chain alkanes **1** taking dodecane as an example:

$C^1H_3–C^2H_2\text{-}C^3H_2\text{-}C^4H_2\text{-}C^5H_2\text{-}(CH_2)_2\text{-}C^{n-4}H_2\text{-}C^{n-3}H_2\text{-}C^{n-2}H_2\text{ -}C^{n-1}H_2\text{-}C^nH_3$

14.10 22.75 32.00 29.45 29.70 29.75 29.70 29.45 32.00 22.75 14.10

3.1.3. Functionalized long-chain 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 $n = m+1$). In spite of the less quantity of functionalized compounds **I** literature data about basic spectral parameters δ^C_i compared with those for alkanes **1** which are given in [2, 3], we examined and analyzed approximately 40 types of such compounds inclusive (to our mind) all main classes of aliphatic compounds. The class of ethyl acetales of the linear aldehydes **38** is only exception by reason of insufficiency literature data about basic spectral parameters $\delta^{C,\mathbf{38}}$.

All compounds **1-37** with different functional groups (including alkanes, when Y = H) are divided into two classes depending on nature of the atom attached to the alkyl chain $CH_3(CH_2)_m$–. The first class denoted as “A” consists of the compounds where carbon atom is attached to the alkyl chain and simultaneously it belongs to the functional group Y. However chemical shifts of such carbon atoms we did not examine.

If heteroatom Z, *i.e.* any other atom except carbon one (including hydrogen atom in alkanes **1**) appears as Y-atom connected with alkyl fragment CH_3-$(CH_2)_m$–, then the compounds of such type will form class "B".

The same as for long-chain alkanes **1** we founded that the values of corresponding parameters δ^C_i are constant in spectra of all types of functionalized long-chain compounds **2-37** within the limits of accepted accuracy. It means that inside every homologous row for the compounds with the same Y value (but different m value) the corresponding parameters $\Delta\delta^C_r$ and $\Delta\delta^C_s$ are practically the same. Therefore it is advisable to determine their average values closely approximated the boundary values inside the row. For all functionalized compounds **2-37** parameters δ^C_r and $\Delta\delta^C_r$ of the molecule **I** "methyl" end are equal to the parameters δ^C_r and $\Delta\delta^C_r$ of long-chain alkanes **1** within the range of accepted accuracy (0.05 ppm) and were given in Table 1. Therefore Table 2 represents only averaged increments $\Delta\delta^C_s$ calculated by formula (5):

$$\Delta\delta^C_s = \delta^C_s - \delta^C_t \qquad (5)$$

Table 2

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

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	6					-0.05	-0.15	-0.50	-0.70	+4.15
6	-C≡CH	8			-0.05	-0.10	-0.15	-0.55	-0.90	-1.15	-11.30
7	-C_6H_5	7				-0.05	-0.10	-0.15	-0.35	+1.80	+6.30
8	-C≡N	8			-0.10	-0.20	-0.40	-0.95	-1.05	-4.30	-12.65
9	-CH=O	8			-0.05	-0.10	-0.20	-0.35	-0.50	-7.60	+14.20
10	-C(CH_3)=O	8			-0.05	-0.10	-0.20	-0.25	-0.50	-5.80	+14.10
11	-C(C6H5)=O	8			-0.05	-0.10	-0.20	-0.25	-0.35	-5.30	+8.90
12[6]	-C(NH_2)=O	6			?	?	-0.20	-0.35	-0.45	-4.10	+6.25
13	-C(OH)=O	8			-0.05	-0.10	-0.25	-0.45	-0.65	-5.05	+4.35
14	-C(OCH_3)=O	8			-0.05	-0.10	-0.20	-0.40	-0.50	-4.70	+4.40
15	-C(OC_2H_5)=O	8			-0.05	-0.10	-0.20	-0.40	-0.50	-4.70	+4.65
16	-C(Cl)=O	8			-0.05	-0.15	-0.35	-0.65	-1.25	-4.65	+17.40

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

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

The compounds of “A” class are given in the table at first, and then compounds of “B” class (including repeated data for alkanes **1**). In contrast to alkanes **1** the number of carbon atoms *s* near the functional group Y in the functionalized compounds **2-37** (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 was found in alkyliodides (**37**).

Above-mentioned increments $\Delta\delta^C_s$ are averaged and have approximate values. The latter ones (by our estimation) may vary within the limits of ± 0.05 ppm. The calculation procedure is described below taling iodoalkanes **37** as an example.

1. For all long-chain homologues of the same type, *e.g.* iodides **37** (where Y = I), which data for $\Delta\delta^C_i$ parameters are given in [2, 3] the value of every increments $\Delta\delta^C_s$ was calculated by formula (5). 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: +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]); +3.90 ppm (1-iodoctadiene, 25 MHz [2]) and +3.85 ppm (1-iodododecane, 75 MHz, [3]).

2. 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 (7) and (8) to "check" the calculation of the basic spectral parameter δ^{C}_{i}. The calculations were done for all "medium-chain" compounds (see below), 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 was entered to the table 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.

It should be noted that all $\Delta\delta^{C}_{s}$ increments which have absolute values equal to 0.05 ppm were entered as a result of checking and updating of the basic spectral parameters δ^{C}_{i} calculations for "medium-chain" compounds.

3.2. Peculiarities of the Basic Spectral Parameters δ^{C}_{i} of "Medium-Chain" and "Short-Chain" Functionalized Compounds I

A bulk of compounds **I** should be divided into three parts depending upon the alkyl chain length. As state above if the amount of hydrogen atoms in the chain satisfies Eq. (1), *i.e.* at $n > r+s \Rightarrow t > 0$, then the compounds are called as long-chain. The "medium-chain" (with the alkyl chain length of 5–10 or even 13 carbon atoms, see above) and "short-chain" (2–4 carbon atoms, see below) compounds are those linear compounds of the general formula **I**, where medium methylene groups $(-CH_2-)_t$ are absent, *i.e.* $(t = 0)^3$, and inequality (6) is realized.

$$m < r + s \qquad (6)$$

It means that a part of carbon atoms in "medium-chain" compounds and all carbon atoms in "short-chain" compounds undergo simultaneous disturbance 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 $-(CH_2)_n-$ 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".

Let us assume that total "disturbance" of the basic spectral parameters δ^{C}_{w}, (denoted as $\Delta\delta^{C}_{w}$) has to be some function of every increments $\Delta\delta^{C}_{r}$ and $\Delta\delta^{C}_{s}$. Let us do the second important assumption. We assume that the effect of one increment on the chemical shift δ^{C}_{w} is independent of the other increment. It means that their total effect, *i.e.* $\Delta\delta^{C}_{w}$ is equal to the total effect of every two increments (Eq. 7):

$$\Delta\delta^C_w = \delta^C_w - \delta^C_t = \Delta\delta^C_r + \Delta\delta^C_s \qquad (7)$$

By using increments $\Delta\delta^C_r$ and $\Delta\delta^C_s$ which are given in Tables 1 and 2, as well as formula (8) derived from the formula (7), we can calculate **all** values of every basic spectral parameters δ^C_w for every medium- and short-chain functionalized compounds **I** containing **all** types of substituents Y (compounds **3-37**).

$$\delta^C_w = \delta^C_t + \Delta\delta^C_r + \Delta\delta^C_s \qquad (8)$$

For the majority of medium-chain compounds **I** we receive very good coincidence of the calculated values δ^C_w with the experimental basic spectral parameters δ^C [2, 3]. Just these calculations were used to ascertain $\Delta\delta^C_s$ values given in Table 2. As an example we give below the calculation by formula (8) for 8 values of δ^C_w for 1-iodoctane (octyliodide) and compare it with experimental values (fig 2). It should be noted that the difference between calculated and experimental values of parameter δ^C_i (*i.e.*$\delta^C_{i,calc.}$- $\delta^C_{i,exp.}$) does not exceed 0.05 ppm by absolute value in any case.

Fig. 2

$\boldsymbol{\delta^C_t}$		29.75	29.75	29.75	29.75	29.75	29.75	29.75	29.75	
$\boldsymbol{\Delta\delta^C_r}$		−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**
$\boldsymbol{\Delta\delta^C_s}$	-0.05	-0.05	−0.10	−0.20	−0.30	−1.20	+0.80	+3.90	−22.60	
$\boldsymbol{\delta^C_{w,calc}}$		14.05	22.65	31.80	29.15	28.50	30.55	33.65	7.15	
$\boldsymbol{\delta^C_{w,exp.}}$		**14.07**	**22.63**	**31.77**	**29.10**	**28.53**	**30.54**	**33.61**	**7.15**	
Difference		**-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 formula (8) values $\delta^C_{w,calc}$ from experimental chemical shifts $\delta^C_{w,exp.}$ does not exceed 0.1 ppm in 95% of the cases. The same calculations for medium-chain (n = 4–8) alcohols, esters and tosilates were published earlier [4].

For short-chain compounds **I** (n = 4 or 3) the deviation value is sometimes 0.5 ppm. And for the compounds **I** with very short chain (n = 2, m = 1) or even without the chain (n = 1, m = 0; for example it is methyliodide in a 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.

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

4. Conclusions

We suggested the new method of calculations all spectral changes occurring in NMR ^{1}H and ^{13}C spectra at the introduction of various substituents Y in the molecule of reference substance – linear alkane. The suggested conception assumed that during transformation of the hypothetical alkane molecule H-$(CH_2)_k$–$(CH_2)_m$–$(CH_2)_l$–Y (**II**) with infinitely long hydrocarbon chain-$(CH_2)_k$– and –$(CH_2)_l$– into the real substance $CH_3(CH_2)_m$Y (**I**) (**II** → **I**), it is necessary to changed fragment –$(CH_2)_k$– for the methyl group, and fragment –$(CH_2)_l$– for the functional group Y. We assume that all carbon atoms in the compound **II** are in the same chemical surroundings and so they have the same values parameter $\delta^C_{hyp.}$, which we take equal to values of the middle methylene groups of long-chain alkanes (δ^C_{hyp}= δ^C_t = 29.75 ppm). The change of δ^C_i value for all or some carbon atoms of fragment $(CH_2)_m$ should take place as a result of transfer (**II** → **I**).

The differences between every carbon parameters (δ^C_i) in **I** and hypothetical value $\delta^C_{hyp.}$ = 29.75 ppm **(**denoted as "increments $\Delta\delta^C_i$") were calculated and tabulated. To a first approximation it may be assumed that both type "disturbance" causes independent effect on δ^C_i of every carbon atoms. In case of long-chain molecules the every carbon atom undergoes one or none "disturbing factor", depending on atom position (at the beginning, in the middle or at the end of the chain). In case of medium- and short-chain compounds **I** values δ^C_w of every *w* carbon atoms of the alkyl chain undergo one or two "disturbing factors" directed from both end of the chain, *i.e.* their total effect is additive. By using aforesaid increments $\Delta\delta^C_i$ we can calculate **all** values of every parameters $\delta^C_{i,calc}$ for long-, medium- and short-chain compounds **I** containing **all** 38 types of substituents Y. In short-chain compounds **I** with $m< 5$ the other indefinite factors additively influenced the values of the basic spectral parameters δ^C, worsening coincidence between calculated $\delta^C_{i,calc}$ and experimental $\delta^C_{i,exp}$ parameters.

The good coincidence between calculated $\delta^C_{i,calc}$ and experimental $\delta^C_{i,exp}$ parameters for long- and medium-chain compounds **I** allows to predict with high admissibility the values of the basic spectral parameters δ^C_i for those compounds **I,** NMR ^{13}C spectra of which are not given in the literature.

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