

"Spherical" organic compounds.

I. Peculiar properties of «spherical» (ball-shaped) pentanes ^1H NMR Spectra.

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November 2016

Abstract. We propose the concept of the spherical (or «ball-shaped») compounds. In this communication we are considered NMR ^1H spectra of 53 «spherical pentanes» - saturated hydrocarbons with a maximum length of the chain of five carbon atoms [from simplest n-pentane to most complicated tetra-(tert-butyl)methane]. The conception of the spherical alkane structure includes: a) a central carbon atom of the whole molecule (C^3); b) two, three or four carboncontaining branches attached to it. These include monocarbonic methyl (Me) and dicarbonic (longest chain) Et, Pr^1 , Bu^1 - fragments; c) one or two branches may be the hydrogen atoms. The central atom (C^3) is surrounded by three layers, called: a) inner - α -layer, b) intermediate - β -layer, and c) the outer - γ -layer, which is often referred to - ω -layer. The inner and intermediate layers may contain both carbon and hydrogen atoms, but the outer layer contain only hydrogen atoms. We consider several types of alkanes sphericity: «quasi-spherical», «minimally-spherical», and «maximally-spherical», as well as linear (n-pentane) and «quasi-linear». The values of proton chemical shifts in spherical alkanes depend on the location of the studied hydrogen atoms in a certain layer. The number of hydrogen atoms in the outer ω -layer (\mathbf{H}_ω) and the uniformity of their distribution in the volume of this outer layer (which depends on the type of alkane sphericity) have a significant influence on the proton chemical shifts. When parameter $\mathbf{H}_\omega = 12$ (or 15) we observe the maximal upfield signals shift of all studied protons (except the methyne hydrogens of isopropyl group). With further growth of \mathbf{H}_ω an increase of the chemical shifts (downfield shift) observed. When $\mathbf{H}_\omega = 12$ (or 15) for the methyl groups of ethyl fragments in the maximally-spherical compounds observed the highest upfield shift. The same applies to methylene groups of ethyl fragments.

To explain these results, the hypothesis, assuming the interaction to each other of three (or especially four) carboncontaining branches, radiating from the central carbon atom C^3 in spherical molecules proposed. This interaction, in our opinion, causes the observable upfield shift of the methyl, methylene or methyne proton's signals and is similar to the proposed earlier interaction of two or three heteroatoms in the case of «anomeric effect» in CHXYZ compounds with gem-location of heteroatoms \mathbf{X} , \mathbf{Y} , \mathbf{Z} .

Key words: «spherical («ball-shaped») pentanes»; central carbon atom of molecule (C^3); carboncontaining branches; ω -layer; types of alkanes sphericity: «quasi-spherical», «minimally-spherical», and «maximally-spherical», number of hydrogen atoms in the outer ω -layer (\mathbf{H}_ω).

I. Introduction.

In the previously articles [1, 2] we have tried to critically comprehend the previously found dependences of hydrogen atoms (protons) chemical shifts in the saturated mono- and polymethylsubstituted linear alkanes. Moreover, not all changes in the chemical shifts of the investigated signals of the methyl ($\delta^{\text{H}}_{\text{CH}_3}$), methylene ($\delta^{\text{H}}_{\text{CH}_2}$) and methine ($\delta^{\text{H}}_{\text{CH}}$) protons, especially in polymethylsubstituted linear alkanes, appears to us obvious.

A systematic review of the alkanes ^1H NMR spectra, which are listed in the sources [3, 4] we use, has led to the fact that in the articles [1, 2] along with the «true linear» long-chain alkanes we have examined the spectra of alkanes, which we called as «branched». To this category of molecules we include, in particular, the «short-chain» alkanes, carbon chain length of which not exceeds more than 5 C atoms. This carbon chain contains one, two or three methyl substituents at one or more of the «mid» carbon atoms C^2 , C^3 or C^4 . That is, in fact, it is a **mono- or polymethylsubstituted pentanes**.

We have included the compounds of such structure into this study of ^1H NMR spectral features of so-called «spherical» (or «ball-shaped») saturated alkanes. Our results suggest that **based on the peculiarities of the studied alkane structure we can predict** at a sufficiently high degree of accuracy **the proton chemical shifts values (δ^{H}) for all saturated alkanes with a chain length of more than 5 carbon atoms also.**

I. 1. Definition of terms used.

Let us introduce the definition of the terms used. The term «**ball-shaped alkanes**» (or «**spherical alkanes**») that studied in this paper, we understand the totality of 53 shown below molecules of saturated alkanes from C_5H_{12} to $\text{C}_{17}\text{H}_{36}$. In these substances, the longest alkyl chain has only five carbon atoms and therefore the center of such a molecule coincide with the C^3 carbon atom of the carbon chain. This atom C^3 called «the **central carbon atom**». Let us consider those 4 alkyl fragments (or a hydrogen atoms), with which this **central carbon atom** is bonded with simple C-C or C-H bonds. Most often we use for these 4 substituents, the term «**branch**», radiating from the center of the molecule. By definition, in order to form the longest five-carbon alkyl chain (or one of several of the most long alkyl chains), two of the four branches should be «**long**» - ie, **dicarbonic alkyl fragments**. We postulated that in these our «spherical alkanes» two remaining valences of the central atom C^3 may form any simple C-C or C-H bonds with two remaining branches

Putting it together. Fragments (branches) can be: 1) long **dicarbonic alkyl fragments** (at least two pieces in every alkane molecule); 2) short **monocarbonic alkyl moiety - methyl group**; 3) carbon-free fragment - hydrogen atom (designated by symbol «**0**»). In first two cases, both types of fragments are named as «**carbonic fragments or carboncontainsng fragments**» and indicated by «**B**» and «**b**», respectively (from the English word «branch»): «**B**» represents one of the three types of dicarbonic alkyl fragments (see below), and «**b**» - monocarbonic alkyl moiety - methyl group].

We have considered all of three possible long dicarbonic fragments «**B**»: 1) **ethyl group**, 2) **isopropyl group** and 3) **tert-butyl group**. These three types of branches (with the addition of two short fragments above - the methyl group «**b**» and the hydrogen atom «**0**») – are those **5 types of substituents**, connected with the central atom C^3 , that are subject to our review. We designated them by common symbol «**n**». Let us lined up all of these substituents in the «hierarchical» series to a four-digit number for every spherical alkanes in such a way that the numeral was the highest value. The most complicated substituent is tert-butyl group – (**Bu**^t or simply «**Bu**» - indicated at numeral 4 «**n** = 4»), which show the number of carbon atoms in a substituent. Further, **Bu** > **Pr**ⁱ (simply «**Pr**», **n** = 3) > **Et** (**n** = 2) > **Me** (**n** = 1) > **H** (**n** = 0).

As mentioned above, all discussed «spherical» saturated alkanes can be viewed as **substituted methane molecule, carbon atom of which** is the above mentioned **central atom C^3** (of **ball-shaped alkane**) provided that **at least two (of 4) substituents (branches) are long dicarbonic**

alkyl fragments «B». As result, we get the substituted pentane ball-shaped molecule under review. Varying all 4 substituents (branches) in the molecules of this structure, we found those 53 theoretically possible compounds, that satisfy the specified constraints. To encode these compounds we used above substituents numerals. The principle of encoding each molecule as the methane molecule substituted with four substituents, the following: 1) The code consists of 4 digits ($n^1n^2n^3n^4$), according to the numeral number of each substituents on the central atom C^3 ; 2) The numerals are arranged from right to left by abovementioned «hierarchical» principle, i.e., decreasing their value ($n^1 \geq n^2$, etc.).

Given the fact that 2 of the 4 substituents should be long **dicarbonic alkyl fragments «B»** (ie, $n^i = 2, 3$ or 4), the smallest number that is encoded each of the 53 considered «spherical» saturated alkane is **2200** and the largest number is **4444**.

Some of 53 disputed compounds yet correct to consider, as linear alkanes. Of course, this is n-pentane (**2200**) containing no alkyl substituents at C^2 , C^3 or C^4 , and is therefore the «true» linear unbranched alkane (not «**spherical alkanes**»). In five compounds, namely, 2-methylpentane (**3200**), 2,2-dimethylpentane (**4200**), 2,4-dimethylpentane (**3300**), 2,2,4-trimethylpentane (**4300**) and 2,2,4,4-tetramethylpentane (**4400**) the branching (methyl group) are present, but not at the central C^3 -atom, (ie, at atoms C^2 and/or C^4). These five compounds, as mentioned above, we propose to give the name of «conditionally linear» or «**quasi-linear**». Again emphasize: these compounds, by definition, are not «**spherical alkanes**». Correctly assume them as branched at the beginning or end of the carbon chain linear alkanes. However, in order to perform the preservation of the systematicity of analysis, these compounds we also included among the considered molecules of «**spherical alkanes**» as «**quasi-linear**» alkanes. So, we call this type of «unspherical alkanes», as «**quasi-linear**» (abbreviated, **L**; labeled as "00").

All combinations of substituents n^i (n^1, n^2, n^3, n^4) at the central carbon atom C^3 lead to the need to divide the 53 compounds considered by several types according to the degree of «**sphericity of their form**».

Thus, «true spherical shape» has, in our opinion, only one of these 53 compounds, namely - tetra-tert-butylmethane (**4444**), 17 carbon atoms of which have a diamond-like structure, and 36 hydrogen atoms occupy the places, which in the diamond would occupy carbon atoms. Generally, «**truly spherical alkanes**» we mean those compounds in which **all 4 substituents** at the central carbon atom C^3 is long dicarbonic alkyl fragments [**B**, i.e., $n^1, n^2, n^3, n^4 = Et, Pr^i$ or Bu^t (or **2, 3, 4**)]. Let us designate this type of «**spherical alkanes**» as maximally spherical (abbreviated, **Max**).

«**Minimally spherical**» (**Min**) we have called the second by decreasing extent of «sphericity» type of alkanes **with the same four carbonic branches** (ie, $n^3 \neq 0$ and $n^4 \neq 0$). Among these **four carbonic branches one (or two)** are short, i.e., methyl groups (n^3 and/or $n^4 = 1$). Depending on the number of methyl groups among these two branches the "minimally spherical" type of alkanes is divided into two subtypes: (**MinI**) and (**MinII**). In subtype **MinI** enter alkanes with both short carbonic branches, i.e., methyl groups; them we also refer to as «**bb**». Subtype **MinII** include alkanes having one short carbonic branch (methyl group), and the second - long one (**Et, Prⁱ** or **Bu^t**). They are designated as "**Bb**".

And finally, «**quasi-spherical**» type of spherical substances we call alkanes with only **three carbonic branches**, and the fourth branch is hydrogenic one (**H** atom, $n^4 = 0$), i.e., it contains no carboncontaining substituents. Designate them as «**Q**»; This type is also divided into two subtypes: (**QI**) and (**QII**). If third carbonic branch is a methyl group ($n^3 = 1$), this type of «**quasi-spherical**» alkanes we call **QI** and denote **b0**. If the third carbonic branch is «long» (**Et, Prⁱ** or **Bu^t**), this type of «**quasi-spherical**» alkanes called **QII**, denoted **B0**.

As mentioned above, along with the true linear n-pentane (**2200**) as «quasi-linear» alkanes we consider the compounds **3200, 4200, 3300, 4300** and **4400**, in which n^3 and / or $n^4 = 0$. In general their code written as: n^1n^200 , and they are indicated by the numeral «00».

Thus, the totality of the 53 «spherical» saturated alkanes under consideration conditionally divided into 4 groups (types). List them, starting with the least degree of sphericity

1) **6** «quasi-linear» compounds (**L**). These are: **1** «truly linear» alkane - n-pentane (**2200**), where n^1 and $n^2 = 2$ (**Et**), and n^3 and $n^4 = 0$ (**H**); and **5** «quasi-linear» alkanes where [n^1 and / or $n^2 = 2, 3$ or **4**]; and n^3 and $n^4 = 0$]; these are 5 compounds: **3200, 4200, 3300, 4300** and **4410**. Their general designations are: «**L, 00**».

2) **16** «Quasi-spherical» alkanes (**Q**), which are divided into 2 groups (**2a** and **2b**) depending on the structure of the substituent n^3 .

2a) 6 «Quasi-spherical» I compounds, **QI**, where $n^3 = b$ (**1**), and $n^4 = 0$. They are: **2210, 3210, 3310, 4210, 4310** and **4410**; the designations employed: «**QI, b0**».

2b) 10 «Quasi-spherical» II compounds, **QII**, where $n^3 = B$, and $n^4 = 0$. They are: **2220, 3220, 3320, 3330, 4220, 4320, 4330, 4420, 4430** and **4440**; the designations employed: «**QII, B0**».

3) **16** «Minimally spherical» alkanes **Min**, which are divided into two subgroups (**3a** and **3b**) depending on the structure of substituent n^3 .

3a) 6 «Minimally spherical» I compounds, **MinI**, where ($n^3 = b$ and $n^4 = b$). They are: **2211, 3211, 3311, 4211, 4311** and **4411**; the designations employed: «**MinI, bb**».

3b) 10 «Minimally spherical» II compounds, **MinII**, where ($n^3 = B$ and $n^4 = b$). They are: **2221, 3221, 3321, 3331, 4221, 4321, 4331, 4421, 4431** and **4441**; the designations employed: «**MinII, Bb**».

4) **15** «Maximally spherical» alkanes **Max**, among which **one** is «truly spherical» alkane - **4444**. These compounds are: **2222, 3222, 3322, 3332, 3333, 4222, 4322, 4332, 4333, 4422, 4432, 4433, 4442, 4443** and **4444**; the designations employed: «**Max, BB**».

Let us illustrate the use of symbols received on the first six compounds where the most complex substituent is an ethyl group ($n^1 = 2$). The simplest of these is the «true linear» n-pentane (**L**) - (it is considered as disubstituted methane – diethylmethane, so it designated code is **2200**). The next in this series is «quasi-spherical» I (**QI**) 3-methylpentane **2210**. Next come the «minimally spherical» I (**MinI**) 3,3-dimethylpentane **2211**, next - «quasi-spherical» II (**QII**) triethylmethane **2220**; next - «minimally spherical» II (**MinII**), methyltriethylmethane **2221** and, finally, «maximally spherical» (**Max**) tetraethylmethane (**2222**). Similarly designated 16 compounds in which the most complicated substituent is an isopropyl group ($n^1 = 3$) [from (2-methylpentane (**3200**) to tetra-isopropylmethane (**3333**)] and also 31 compound with most complicated branch - t-butyl group ($n^1 = 4$) [from 2,2-dimethylpentane (**4200**) to tetra-tert-butylmethane (**4444**)].

Let us note that not all of these 53 compounds considered here currently known; probably some of them can not generally be stable in the usual conditions (for example, tetra-tert-butylmethane **4444**). Moreover, not for all known stable compounds we found and discussed the ^1H NMR spectra.

I. 2. Graphical representation of « spherical alkanes ».

We imagine an imaginary ideal spatial structure of each of spherical alkanes, as a system of concentric hollow spheres placed one into the other. (A descriptive analogy is a Russian «matryoshka» toy). In the center of the whole structure of every spherical alkane is the smallest in size ball - the central atom C^3 . Around it is located next to the central atom C^3 concentric hollow sphere, called the «**inner layer**» or « **α - layer**». His «cover» a larger-sized second concentric hollow sphere, called the **intermediate layer** or « **β - layer**». Finally, the « **β - layer**» «covered» by an even greater by size third concentric hollow ball, which is called the **outer layer**. This outer layer logically designate as « **γ - layer**». However, more often we call it « **ω - layer**», as in the structure of spherical alkanes we are considering (pentanes) it is the last layer.

In the cutaway the entire structure of every spherical alkane is a spherical three concentric circles located around the central atom C^3 . For the graphical convenience, we will replace the usual

concentric circles by squares. Then each of the 53 considered compounds will appear schematically as three «concentric» squares outlined by dashed lines. Each «concentric square» depicts one of the layers of spherical alkane.

Drawing the dotted lines on both diagonals in all three squares, we get 4 sectors. In each of these sectors we put one of the four branches of a substituted methane, how we imagine the «spherical alkane». The first (lowest, small) square represents the **inner layer**, ie, « **α - layer**». In each sector of the **first square** we introduced those atoms of each of the 4 branches of a molecule, designated as C^2 -, C^4 - or H^3 - atoms of pentane molecules, which are bound to the central atom C^3 . Place each of these atoms **on the abscissa or ordinate axis**, and connect it with central atom C^3 by a straight line (**chemical bond**). Among the hydrogen atoms we study in the **α - layer** are located **only atoms H^3** bound **to the central atom C^3** .

In each of the sectors of the **second square (intermediate layer)**, we continue each of the 4 branches of the substituent n^i , ie, introduce such atoms: C^1 -, C^5 -, H^2 - or H^4 -atoms of pentane molecule. The carbon atoms C^1 - and / or C^5 -of each long **alkyl** substituents ($n^i = B$) connected with the corresponding chemical bond with carbon atom (C^2 - or C^4 -), which located in the first square. In the case of the «short» branch formed by the **methyl group** ($n^i = b$ or **1**), these **three atoms are hydrogens** (every referred to as H^4 -). In the case of the **ethyl group** ($n^i = 2$) in second square located **two H atoms and one C atom**; in the case of an **isopropyl group** ($n^i = 3$) - two C atoms and one H atom. Finally, in the case of the **tert-butyl group** ($n^i = 4$), these substituents are **three carbon atoms**. Note that for the **hydrogen atom as one of the branches** ($n^i = 0$, where $i = 3$ and / or 4) in the second square (**intermediate layer**), **any substituents in this branch, naturally will be absent**.

In the second square, or «**intermediate**» « **β - layer**» among hydrogen atoms we study there are H atoms which are bonded with C^2 - (or C^4 -) atoms, adjacent to the central atom C^3 , i.e., a) **methyl group** which is short branch - **b** ($n^i = 1$), b) **methylene group** – the part of ethyl moiety (with $n^i = 2$), or c) **methyne hydrogen atom** of isopropyl fragment (with $n^i = 3$).

By the same principle, continuing each of 4 branches (substituents - n^i), fill the **third, most extreme, «outer» - (largest) square**. These atoms linked to the carbon atoms (C^1 and C^5), which located in **β - layer**. In this «**outer** square» («**outer layer**», « **γ - layer**», « **ω - layer**») of course, there **will be no substituents** in case, when the considered branch n^i is a methyl group (ie, $n^i = 1, b$). To another type of branches belong three dicarbonic fragments of substituents «**B**» ($n^i = 2, 3, 4$). In case of ethyl group (**B**, $n^i = 2$) these substituents in **ω - layer** are **three hydrogen atoms**. In the case of isopropyl group (**B**, $n^i = 3$) - also with three hydrogen atoms associated with each of the two carbon atoms, which located in the second square; i.e., a total in **ω - layer** be present **six hydrogen atoms**. Finally, in case of the tert-butyl group (**B**, $n^i = 4$), these substituents are **nine hydrogen atoms** - in threes for each carbon atom from the second «**intermediate**» « **β - layer**» (square). **We emphasize**, that in **ω - layer** are located **hydrogen atoms only**.

Note that the ideal model of spherical alkanes, described above, do not reflect by our opinion the real geometrical dimensions of the molecule. We can assume that the radius of the **α - layer** will be approximately equal to the length of the ordinary C-C bond, ie, approximately 1.5 - 1.6 Angstroms. But the radius of the **β - layer** due to non-linearity of each of four branches of a substituted methane molecule, is expected less than 3 angstroms (which roughly corresponds to twice the length of ordinary C-C bond). Yet more difficult to calculate the radius of **ω - layer**. In reality, in our view, the spherical molecules of alkanes **are not perfect, but deformed spheres**, especially with considering the existing «defects» of the structure of some of them. For example, in «**quasi-spherical**» alkanes (**Q**), one of the branches of which is hydrogen atom, the correct form of the ball is to be distorted by definition.

I. 3. The spectral parameters. Terminology used.

We discuss only the values of the **basic spectral parameters** – proton's chemical shifts in the spherical alkanes PMR spectra. Values of spin coupling constants we have not discussed. We consider the positions of the centers of proton's absorption signals: 1) methyl groups (referred to as $\delta^{\text{H}}_{\text{CH}_3}$), methylene groups ($\delta^{\text{H}}_{\text{CH}_2}$) and methyne groups ($\delta^{\text{H}}_{\text{CH}}$). We use only such **basic spectral parameters**, the values of which have been published in the chemical literature; for each parameter is given a reference to the source of information. In various works for obtaining spectra were used the different solvents, but we do not specify them. If the spectrum of the same substance was obtained in different solvents, then we present the data in CDCl_3 (if present) in the first place. Also, if the spectra of the same substances have been published in the various articles, and numerical data differ, we, first of all, present the data taken from sources [3, 4], which seem to us the most reliable. All alternative numerical data from other sources we do not give here. The selection of the most reliable data obtained from other (not [3] or [4]) references is our subjective preference.

Note that the values of the methyl groups chemical shifts of here discussed spherical (ball-shaped) alkanes vary widely, from about 0.65 ppm to about 1.25 ppm. Chemical shift values of methylene and especially methine groups vary within even more significant ($\sim 0.7\text{ppm}$ to $\sim 2.3\text{ ppm}$).

If two methylene protons (or two methyl groups in the isopropyl moiety) are magnetically non-equivalent, we take as a parameter $\delta^{\text{H}}_{\text{CH}_2}$ ($\delta^{\text{H}}_{\text{CH}_3}$) the arithmetic mean values of these two «magnetically non-equivalent» chemical shifts.

Even more important discussed here values are the **differential spectral parameters**, denoted by us as $\Delta\delta^{\text{H}}$: $\Delta\delta^{\text{H}}_{\text{CH}_3}$, $\Delta\delta^{\text{H}}_{\text{CH}_2}$ and $\Delta\delta^{\text{H}}_{\text{CH}}$. For example, $\Delta\delta^{\text{H}}_{\text{CH}_2}$ parameter represents a **difference** between discussed chemical shift of methylene protons ($\delta^{\text{H}}_{\text{CH}_2}$) in the spherical alkane and received previously [5], the averaged value of the chemical shift of the mid methylene groups in long-chain linear alkanes $\delta^{\text{H, av.}}_{\text{CH}_2} = \mathbf{1.270}$ ppm. This difference for convenience we expressed in bold font, but in billionth's parts (mlrd.), not in ppm. Depending on the sign of this difference in green font are negative values; and in red font - positive values. Zero difference ($\Delta\delta^{\text{H}}_{\text{CH}_2} = 0$) denotes gold (0 mlrd.).

As earlier [6], we take the value of the basic error of spectral parameters δ^{H} measurements equal to **20 mlrd.** Thus $\delta^{\text{H}}_{\text{CH}_2}$ values that are equal to **1.270 ppm \pm 0.020 ppm** (ie, are in a range from **1.250 ppm** to **1.290 ppm**) fall into «band of uncertainty of δ^{H} values» because they are commensurable with the experimental error. The differential parameters $\Delta\delta^{\text{H}}_{\text{CH}_2}$ calculated for these values $\delta^{\text{H}}_{\text{CH}_2}$, will be equal to **± 20 mlrd.** We treated them as «insufficiently justified»; and, therefore, their discussion is not feasible. All this applies also to the parameters of methine protons $\delta^{\text{H}}_{\text{CH}}$ and $\Delta\delta^{\text{H}}_{\text{CH}}$, although their «insufficiently justified» values may differ from values ± 20 mlrd.

For methyl protons the rounded averaged value of terminal methyl groups chemical shift in the long-chain linear alkane $\delta^{\text{H, av.}}_{\text{CH}_3} = \mathbf{0.880}$ ppm [5]. In the present study we adopted for them more narrow «band of uncertainty» equal to **0.875 ppm \pm 0.015 ppm** (ie, from **0.860** to **0.890** ppm). The differential parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ equal to ± 20 mlrd., as in the case of methylene and methine protons, are considered by us as «insufficiently justified»; and therefore are not discussed.

In discussing the differential values of **methyne group** parameters $\Delta\delta^{\text{H}}_{\text{CH}}$ (see below) - we provisionally adopted the following gradation.

«Zero» values (from 0 to ± 50 mlrd.); these values are typed 10 font.

«Small» values (from ± 60 to ± 100 mlrd.); these values are typed 12 font.

«Average» values (from ± 110 to ± 300 mlrd.); these values are typed 14 font.

«Large» values (from ± 310 to ± 500 mlrd.); these values are typed 16 font.

And «Very large» values exceeding the values of ± 500 mlrd., typed 18 type.

For differential parameters of methylene groups - $\Delta\delta^H_{CH_2}$ - we provisionally adopted the following gradation:

«Zero» values (from 0 to ± 20 mlrd.); these values are typed 10 font.

«Small» values (from ± 20 to ± 50 mlrd.); these values are typed 12 font.

«Average» values (from ± 60 to ± 150 mlrd.); these values are typed 14 font.

«Large» values (from ± 160 to ± 300 mlrd.); these values are typed 16 font.

And «Very large» values exceeding the values of ± 300 mlrd., typed 18 type.

For differential parameters of methyl groups - $\Delta\delta^H_{CH_3}$ - we provisionally adopted the following gradation:

«Zero» values (from 0 to ± 20 mlrd.); these values are typed 10 font.

«Small» values (from ± 20 to ± 40 mlrd.); these values are typed 12 font.

«Average» values (from ± 50 to ± 100 mlrd.); these values are typed 14 font.

«Large» values (from ± 110 to ± 200 mlrd.); these values are typed 16 font.

And «Very large» values exceeding the values of ± 200 mlrd., typed 18 type.

All values of differential spectral parameters ($\Delta\delta^H$) rounded to the nearest magnitudes that are aliquot of 0.01 ppm (10 mlrd.).

II. Experimental part.

As stated above, we used only the spectral parameters δ^H , published in the chemical literature [3, 4, 7, 8]. We present these data (including above comments done) separately for each of the 5 above described fragments, composing each of the 4 branches of the considered spherical alkanes. We selected the order of consideration of these fragments as follows. Firstly, we considered «long» dicarbonic fragments «B» of: 1) ethyl, 2) isopropyl, 3) tert-butyl group. Then we considered a «short» monocarbonic fragment «b» - methyl group. And finally, we viewed hydrogen atom H^3 at C^3 «0». For the first two long fragments «B» (ethyl and isopropyl fragments) firstly we considered spectral parameters of the methyl groups located on the «outer» ω - layer, then - the parameters of the methylene group in the ethyl fragments and methyne proton in isopropyl fragments located in the «intermediate» β - layer.

II. 1. Ethyl fragment

Ethyl fragment ($C^1H^1_3-C^2H^2_2$) found in 31 of the 53 compounds under consideration. This compound are **2200, 2210, 2211, 2220, 2221, 2222, 3200, 3210, 3211, 3220, 3221, 3222, 3320, 3321, 3322, 3332, 4200, 4210, 4211, 4220, 4221, 4222, 4320, 4321, 4322, 4332, 4420, 4421, 4422, 4432, 4442**. To emphasize the dominant presence of the ethyl group, the generic code of compounds containing ethyl fragment, we can described as: $2n^2n^3n^4$. At the same time we emphasize that such a designation does not always corresponds the above rules of substituents seniority (since $n^1 = 2 < 3, 4$).

The compounds, for which we have PMR spectra, hereafter in bold; others given in bold italics. At our disposal there are PMR spectral data for 19 of the these possible 31 compounds: **2200, 2210, 2211, 2220, 2221, 2222, 3200, 3210, 3220, 3320, 4200, 4211, 4220, 4221, 4222, 4320, 4321, 4420, 4422**. Absent PMR spectra of the 12 compounds: *3211, 3221, 3222, 3321, 3322, 3332, 4210, 4322, 4332, 4421, 4432, 4442*.

Depending on the structure of the most branched substituent located at the central atom C^3 , the 19 substances for which there is spectral data, includes: a) all 6 of 6 possible substances with ethyl substituent ($n^1 = n^2 = 2$, the generic code is: $22n^3n^4$); b) 4 of 10 compounds with isopropyl

substituent ($n^2 = 3$, the generic code is: $32n^3n^4$) and c) **9** of **15** compounds with a t-butyl group ($n^2 = 4$, the code is: $42n^3n^4$).

All possible substances (31) are divided, according to their «sphericity».

«Quasi-linear» alkanes (**L**) include **three** compounds: **2200, 3200, 4200**.

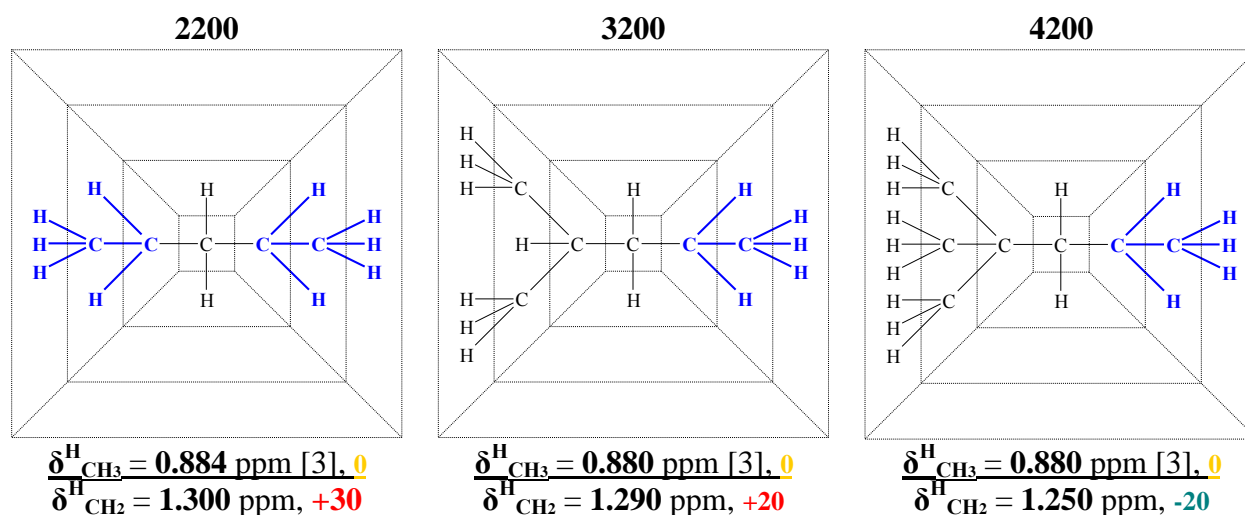
«Quasi-spherical» alkanes (**Q**) are divided into two subgroups: **QI** and **QII**. The **QI** subgroup includes **three** substances with the «short» carbon branch - methyl group: **2210, 3210, 4210**. In **QII** subgroup includes **six** compounds: **2220, 3220, 3320, 4220, 4320, 4420**.

«Minimally spherical» alkanes **Min** is also divided into two subgroups. The first subgroup **MinI** includes **three** substances: **2211, 3211, 4211**. The second subgroup - **MinII** - includes **six** ports: **2221, 3221, 3321, 4221, 4321, 4421**.

Finally, a group of 10 «Maximally spherical» alkanes **Max**. We found PMR spectra for only **three** compounds: **2222, 4222, 4422**.

II. 1. 1. Quasi-linear alkanes (code: $2n^200$).

As stated above these include three compounds in which two of the four substituents are hydrogen atoms, (n^3 and $n^4 = 0$; code: $2n^200$). This are n-pentane (**2200**), 2-methylpentane (**3200**), and 2,2-dimethylpentane (**4200**). Compounds of this group, for which we have no PMR spectra, are absent. We give for these 3 substances the abovementioned schematic square representations. Here (and on) the studied ethyl fragment outlined in bold blue. Below the picture we give the values of the basic spectral parameters (δ^H). The chemical shifts values of the methyl ($\delta^H_{CH_3}$) and methylene ($\delta^H_{CH_2}$) protons of ethyl groups under consideration placed in a fraction. In the case of magnetically non-equivalent methylene protons, as stated above, we give both their values. But the differential parameter ($\Delta\delta^H_{CH_2}$) is calculated using the arithmetic mean values of both methylene protons magnetically nonequivalent chemical shifts numerals. After the numerals of basic spectral parameters (chemical shifts $\delta^H_{CH_3}$ and $\delta^H_{CH_2}$) we give a reference to the literary sources. Then the calculated values of the differential parameter ($\Delta\delta^{Et, \omega-H}_{CH_3}$ and $\Delta\delta^{Et, \beta-H}_{CH_2}$), rounded with the precision up to 10 mlrd., given with colored fonts of different sizes (see. above).



II. 1. 2. «Quasi-spherical Q (code: $2n^2n^30$).

II. 1. 2. 1. «Quasi-spherical QI (code: $2n^210$).

QI subgroup includes two compounds in which the second smallest substituent ($n^3 = 1$) is a methyl group «b» ($n^3 = 1$; code: $2n^210$): 3-methylpentane (**2210**), and 2,3-dimethylpentane (**3210**).

PMR spectrum of alkane **4210** is absent. Hereinafter (except subsection **II. 5. 3.**) we give only spectral data. The schematic square representations omitted.

2210	3210	4210
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.860} \text{ ppm [4], } \mathbf{-20}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.230} \text{ ppm, } \mathbf{-40}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.863} \text{ ppm [3], } \mathbf{-20}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.230} \text{ ppm, } \mathbf{-40}}$	Data absent

II. 1. 2. 2. «Quasi-spherical **QII** (code:2n²20).

The spectral data of all six compounds **QII** (2220, 3220, 4220, 3320, 4320 and 4420) are given.

2220	3220	4220
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.837} \text{ ppm [3], } \mathbf{-40}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.278} \text{ ppm, } \mathbf{+10}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.856} \text{ ppm [3], } \mathbf{-20}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.260} \text{ ppm, } \mathbf{-10}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.920} \text{ ppm [3], } \mathbf{+40}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.290} \text{ ppm, } \mathbf{+20}}$
3320	4320	4420
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.904} \text{ ppm [3], } \mathbf{+20}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.250} \text{ ppm, } \mathbf{-20}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.960} \text{ ppm [7], } \mathbf{+80}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{(1.315?)^*} \text{ ppm, } \mathbf{+45?}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.970} \text{ ppm [7], } \mathbf{+90}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.310} \text{ ppm, } \mathbf{+40}}$

* The mean value of the interval given by authors.

II. 1. 3. «Minimally spherical» compounds, **Min** (code: n¹n²21).

II. 1. 3. 1. «Minimally spherical» I compounds, **MinI** (code:2n²11).

The spectral data of two compounds **MinI** (2211 and 4211) are given. PMR spectrum of alkane **3211** is absent.

2211	3211	4211
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.792} \text{ ppm [3], } \mathbf{-90}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.203} \text{ ppm, } \mathbf{-70}}$	Data absent	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.830} \text{ ppm [7], } \mathbf{-50}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.320} \text{ ppm, } \mathbf{+50}}$

II. 1. 3. 2. «Minimally spherical» II compounds, **MinII** (code:2n²21)

The spectral data of three compounds **MinII** (2221, 4221, and 4321) are given. PMR spectra of alkanes **3221**, **3321**, **4421** are absent.

2221	4221	4321
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.757} \text{ ppm [3], } \mathbf{-120}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.193} \text{ ppm, } \mathbf{-80}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.830} \text{ ppm [7], } \mathbf{-50}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.365} \text{ ppm, } \mathbf{+100}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.870} \text{ ppm [7], } \mathbf{-10}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.42} \text{ ppm, } \mathbf{+150}}$

II. 1. 4. «Maximally spherical» alkanes **Max** (code: n¹n²22).

The group **Max** (n⁴ = 2) included 3 compounds (from 10) for which we have PMR spectra: **2222**, **4222**, **4422**. PMR spectra of alkanes **3222**, **3322**, **4322**, **3332**, **4332**, **4432** and **4442** are absent.

2222	4222	4422
$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.728} \text{ ppm [3], } \mathbf{-150}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.171} \text{ ppm, } \mathbf{-100}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{0.870} \text{ ppm [7], } \mathbf{-10}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.390} \text{ ppm, } \mathbf{+120}}$	$\frac{\delta^{\text{H}}_{\text{CH}_3} = \mathbf{1.020} \text{ ppm [7], } \mathbf{+140}}{\delta^{\text{H}}_{\text{CH}_2} = \mathbf{1.570} \text{ ppm, } \mathbf{+300}}$

II. 2. Isopropyl fragment.

Isopropyl fragment $[(C^1H^1_3)_2C^2H^2-]$, as well as discussed above ethyl fragment, found in 31 of the 53 compounds under consideration. This substances are: **3200, 3210, 3211, 3220, 3221, 3222, 3300, 3310, 3311, 3320, 3321, 3322, 3330, 3331, 3332, 3333, 4300, 4310, 4311, 4320, 4321, 4322, 4330, 4331, 4332, 4333, 4430, 4431, 4432, 4433, 4443.**

To emphasize the dominant presence of isopropyl group the common code of compounds containing isopropyl moiety, can be described as: $3n^2n^3n^4$. At the same time we emphasize that such designation does not always correspond to the rules of precedence above substituents (as $n^1 = 3 < 4$).

At our disposal there are PMR spectral data for 15 of the possible 31 substances: : **3200, 3210, 3220, 3300, 3310, 3311, 3320, 3330, 4300, 4310, 4311, 4320, 4321, 4331, 4430.** PMR spectra of 17 compounds: **3211, 3221, 3222, 3321, 3322, 3331, 3332, 3333, 4322, 4330, 4332, 4333, 4431, 4432, 4433, 4443.** absent for us.

As for the ethyl derivatives, all 31 possible alkanes we divide by the degree of "sphericity".

«**Quasi-linear**» alkanes (**L**) include three compounds: **3200, 3300, 4300.**

«**Quasi-spherical**» «alkanes (**Q**) are divided into two subgroups: **QI** and **QII**. The **QI** subgroup includes **three** substances with the "short" carbon branch - methyl group: **3210, 3310, 4310.**

QII subgroup includes **six** compounds: **3220, 3320, 3330, 4320, 4330, 4430.**

«**Minimally spherical**» alkanes **Min** is also divided into two subgroups. The first subgroup **MinI** includes **three** substances: **3211, 3311, 4311.** The second subgroup - **MinII** - includes **six** alkanes: **3221, 3321, 4321, 3331, 4331, 4431.**

Finally, in the group of 10 «**Maximally spherical**» alkanes **Max** we found no one PMR spectra for any compounds: **3222, 3322, 4322, 3332, 4332, 4432, 3333, 4333, 4433, 4443.**

II. 2. 1. Quasi-linear alkanes (code: $3n^200$).

These include three compounds: 2-methylpentane (**3200**), 2,4-dimethylpentane (**3300**), and 2,2,4-trimethylpentane (**4300**). For all compounds NMR spectra were found.

3200 $\delta^H_{CH_3} = 0.864$ ppm [3], -20 $\delta^H_{CH} = 1.541$ ppm, +270	3300 $\delta^H_{CH_3} = 0.853$ ppm [3], -30 $\delta^H_{CH} = 1.619$ ppm, +350	4300 $\delta^H_{CH_3} = 0.907$ ppm [3], +30 $\delta^H_{CH} = 1.657$ ppm, +390
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II. 2. 2. «Quasi-spherical **Q** (code: $3n^2n^30$).

II. 2. 2. 1. «Quasi-spherical **QI** (code: $3n^210$).

QI subgroup includes three compounds in which the second smallest substituent ($n^3 = 1$) is a methyl group «b» (code: $3n^210$): 2,3-dimethylpentane (**3210**), 2,3,4-trimethylpentane (**3310**) and 2,2,3,4-tetramethylpentane (**4310**). Compounds of this subgroup, for which we have no NMR spectra, absent.

3210 $\delta^H_{CH_3} = 0.856$ and 0.796 ppm, round. aver. value. 0.830 ppm [3], -50 $\delta^H_{CH} = 1.560$ ppm, +290	3310 $\delta^H_{CH_3} = 0.882$ and 0.798 ppm, round. aver. value. 0.840 ppm [3], -40 $\delta^H_{CH} = 1.639$ ppm, +370	4310 $\delta^H_{CH_3} = 0.882$ and 0.782 ppm, round. aver. value. 0.830 ppm [3], -50 $\delta^H_{CH} = 1.974$ ppm, +700
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II. 2. 2. «Quasi-spherical» **QII** (code:3n²20).

The spectral data of five from six compounds **QII** (3220, 3320, 3330, 4320, 4330 and 4430) are given. PMR spectrum of alkane 4330 is absent.

3220 $\delta^{\text{H}}_{\text{CH}_3} = 0.828$ ppm [3], -50 $\delta^{\text{H}}_{\text{CH}} = 1.690$ ppm, +420	3320 $\delta^{\text{H}}_{\text{CH}_3} = 0.876$ и 0.845 ppm, round. aver. value <u>0.860</u> ppm [3], -20 $\delta^{\text{H}}_{\text{CH}} = 1.740$ м.д., +470	4320 $\delta^{\text{H}}_{\text{CH}_3} = 0.880$ и 0.860 ppm, round. aver. value <u>0.870</u> ppm [7], -10 $\delta^{\text{H}}_{\text{CH}} = 2.000$ м.д., +730
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3330 $\delta^{\text{H}}_{\text{CH}_3} = 0.940$ ppm [8], +50 $\delta^{\text{H}}_{\text{CH}} = 1.890$ ppm, +620	4330 Data absent	4430 $\delta^{\text{H}}_{\text{CH}_3} = 1.150$ ppm [7], +270 $\delta^{\text{H}}_{\text{CH}} = 2.180$ ppm, +910
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* The mean value of the interval given by authors.

II. 2. 3. «Minimally spherical» compounds, **Min** (code: n¹n²31).

II. 2. 3. 1. «Minimally spherical» I compounds, **MinI** (code:3n²11).

The spectral data of two compounds **MinI** (3311 and 4311) are given. PMR spectrum of alkane 3211 absent.

3211 Data absent	3311 $\delta^{\text{H}}_{\text{CH}_3} = 0.806$ ppm [3], -70 $\delta^{\text{H}}_{\text{CH}} = 1.660$ ppm, +390	4311 $\delta^{\text{H}}_{\text{CH}_3} = 0.890$ ppm [7], +10 $\delta^{\text{H}}_{\text{CH}} = 1.810$ ppm, +540
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II. 2. 3. 2. «Minimally spherical» II compounds, **MinII** (code:3n²21)

The spectral data of three of six possible compounds **MinII** (4321, 4331, and 4431) are given. PMR spectra of alkanes 3221, 3321, 3331 absent.

3221 Data absent	3321 Data absent	4321 $\delta^{\text{H}}_{\text{CH}_3} = 0.970$ ppm [7], +100 $\delta^{\text{H}}_{\text{CH}} = 1.910$ ppm, +640
3331 Data absent	4331 $\delta^{\text{H}}_{\text{CH}_3} = 1.000$ и 1.002 ppm, round. aver. value <u>1.010</u> [7], +140 $\delta^{\text{H}}_{\text{CH}} = 2.010$ ppm, +740	4431 $\delta^{\text{H}}_{\text{CH}_3} = 1.160$ ppm [7], +280 $\delta^{\text{H}}_{\text{CH}} = 2.080$ ppm, +810

II. 2. 4. «Maximally spherical» alkanes **Max** (code: n¹n²n³3).

The group **Max** (n⁴ = 3) included 10 compounds. PMR spectra of all these alkanes 3222, 3322, 4322, 3332, 4332, 4432, 3333, 4333, 4433 and 4443 absent.

II. 3. Tert-butyl fragment.

Tert-butyl fragment [(C¹H¹)₃C²⁻], as well as discussed above ethyl and isopropyl fragments, found in 31 of the 53 compounds under consideration. These substances are: **4200, 4210, 4211, 4220, 4221, 4222, 4300, 4310, 4311, 4320, 4321, 4322, 4330, 4331, 4332, 4333, 4400, 4410, 4411, 4420, 4421, 4422, 4430, 4431, 4432, 4433, 4440, 4441, 4442, 4443, 4444**.

To emphasize the dominant presence of tert-butyl group the common code of compounds containing tert-butyl moiety, can be described as: **4n²n³n⁴**. This designation is already conducted according to the rules of precedence substituents.

At our disposal there are PMR spectral data for 19 of the possible 31 substances: **4200, 4211, 4220, 4221, 4222, 4300, 4310, 4311, 4320, 4321, 4331, 4400, 4410, 4411, 4420, 4422, 4430, 4431, 4440**. PMR spectra of 12 compounds: **4210, 4330, 4421, 4441, 4322, 4332, 4432, 4442, 4333, 4433, 4443, 4444** are absent for us.

All 31 possible alkanes we divide by the degree of «sphericity».

«**Quasi-linear**» alkanes (**L**) include **three** compounds: **4200, 4300, 4400**.

«**Quasi-spherical**» alkanes (**Q**) are divided into two subgroups: **QI** and **QII**. The **QI** subgroup includes **three** substances with the «short» carbon branch - methyl group: **4210, 4310, 4410**.

QII subgroup includes **six** compounds: **4221, 4321, 4421, 4331, 4431, 4441**.

«**Minimally spherical**» alkanes **Min** is also divided into two subgroups. The first subgroup **MinI** includes **three** substances: **4211, 4311, 4411**. The second subgroup - **MinII** - includes **six** alkanes: **4221, 4321, 4331, 4421, 4331, 4441**.

The group **Max** included 2 compounds (from 10 possible) for which we have PMR spectra: **4222, 4422**. PMR spectra of alkanes **4322, 4332, 4432, 4442, 4333, 4433, 4443, 4444** are absent.

II. 3. 1. Quasi-linear alkanes (code: 4n²00).

These include three compounds: 2,2-dimethylpentane (**4200**), 2,2,4-trimethylpentane (**4300**), and 2,2,4,4-tetramethylpentane (**4400**). For all these compounds NMR spectra were found.

4200	3300	4300
$\delta^{\text{H}}_{\text{CH}_3} = 0.864$ ppm [3], -20	$\delta^{\text{H}}_{\text{CH}_3} = 0.892$ ppm [3], +10	$\delta^{\text{H}}_{\text{CH}_3} = 0.977$ ppm [3], +100

II. 3. 2. «Quasi-spherical Q (code:4n²n³0).

II. 3. 2. 1. «Quasi-spherical QI (code:4n²10).

QI subgroup includes two compounds: 2,3-dimethylpentane (**3210**), 2,2,3,4-tetramethylpentane (**4310**) and 2,2,3,4,4-pentamethylpentan (**4310**). PMR spectrum of alkane **4210** absent.

4210	4310	4410
Data absent	$\delta^{\text{H}}_{\text{CH}_3} = 0.873$ ppm [3], -10	$\delta^{\text{H}}_{\text{CH}_3} = 0.980$ ppm [7], +100

II. 3. 2. 2. «Quasi-spherical QII (code:4n²20).

The spectral data of five from six compounds **QII** (**4220, 4320, 4420, 4330, 4430** and **4440**) are given. PMR spectrum of alkane **4330** absent.

4220	4320	4420
$\delta^{\text{H}}_{\text{CH}_3} = 0.850$ ppm [3], -30	$\delta^{\text{H}}_{\text{CH}_3} = 0.890$ ppm [7], +10	$\delta^{\text{H}}_{\text{CH}_3} = 0.980$ ppm [7], +100

4330	4430	4440
Data absent	$\delta^{\text{H}}_{\text{CH}_3} = 1.150 \text{ ppm [7] } +270$	$\delta^{\text{H}}_{\text{CH}_3} = 1.230 \text{ ppm [7] } +350$

II. 3. 3. «Minimally spherical» compounds, **Min** (code: n^1n^241).

II. 3. 3. 1. «Minimally spherical» I compounds, **MinI** (code: $4n^211$).

The spectral data of all three compounds **MinI** (4211, 4311, 4411.) are given.

4211	4311	4411
$\delta^{\text{H}}_{\text{CH}_3} = 0.860 \text{ ppm [7], } -20$	$\delta^{\text{H}}_{\text{CH}_3} = 0.900 \text{ ppm [7], } +20$	$\delta^{\text{H}}_{\text{CH}_3} = 0.990 \text{ ppm [7], } +110$

II. 3. 3. 2. «Minimally spherical» II compounds, **MinII** (code: $4n^2n^31$).

The spectral data of four from six possible compounds **MinII** (4221, 4321, 4331, 4431) are given. PMR spectra of alkanes **4421**, **4441** are absent.

4221	4321	4421
$\delta^{\text{H}}_{\text{CH}_3} = 0.860 \text{ ppm [7], } -20$	$\delta^{\text{H}}_{\text{CH}_3} = 0.930 \text{ ppm [7], } +50$	Data absent
4331	4431	4441
$\delta^{\text{H}}_{\text{CH}_3} = 0.990 \text{ ppm [7], } +110$	$\delta^{\text{H}}_{\text{CH}_3} = 1.080 \text{ ppm [7] } +200$	Data absent

II. 3. 4. «Maximally spherical» alkanes **Max** (code: n^1n^244).

The group **Max** ($n^4 = 4$) included 2 compounds (from 10) for which we have PMR spectra: **4222**, **4422**. PMR spectra of 8 alkanes (**4222**, **4322**, **4422**, **4332**, **4432**, **4442**, **4333**, **4433**, **4443**, **4444**) absent.

4222	4422
$\delta^{\text{H}}_{\text{CH}_3} = 0.910 \text{ ppm [7], } +30$	$\delta^{\text{H}}_{\text{CH}_3} = 1.060 \text{ ppm [7] } +180$

II. 4. Methyl fragment.

Methyl fragment C^2H_3 - found in 22 of the 53 compounds under consideration. These substances are: **2210**, **2211**, **2221**, **3210**, **3211**, **3221**, **3310**, **3311**, **3321**, **3331**, **4210**, **4211**, **4221**, **4310**, **4311**, **4321**, **4331**, **4410**, **4411**, **4421**, **4431**, **4441**.

To emphasize the dominant presence of methyl group the common code of compounds containing methyl moiety, can be described as: $1n^2n^3n^4$. We emphasize that such a designation does not correspond to the rules of precedence above substituents (as $n^1 = 1 < 2, 3, 4$).

At our disposal there are PMR spectral data for 15 of the possible 22 substances: **2210**, **2211**, **2221**, **3210**, **3310**, **3311**, **4211**, **4221**, **4310**, **4311**, **4321**, **4331**, **4410**, **4411**, **4431**. PMR spectra of 7 compounds: **3211**, **3221**, **3321**, **3331**, **4210**, **4421**, **4441** are absent for us.

All 22 possible alkanes we divide by the degree of «sphericity».

Because of the structure peculiarities of the compounds in question are absent such groups of «spherical» alkanes as «quasi-linear» alkanes (**L**), «quasi-spherical» alkanes (**QII**) and «maximally spherical» alkanes **Max**.

«Quasi-spherical» «alkanes of subgroup (**QI**) includes six substances: **2210**, **3210**, **3310**, **4210**, **4310**, **4410**.

«Minimally spherical» alkanes of the first subgroup **MinI** includes six substances also: **2211**, **3211**, **3311**, **4211**, **4311**, **4411**. The second subgroup - **MinII** - includes ten alkanes: **2221**, **3221**, **3321**, **3331**, **4221**, **4321**, **4331**, **4421**, **4431**, **4441**. We have PMR spectra of 5 compounds (from 10 possible): **2221**, **4221**, **4321**, **4331** and **4431**. PMR spectra of alkanes **3221**, **3321**, **3331**, **4421** and **4441** are absent.

II. 4. 1. «Quasi-spherical alkanes **Q** (code: $n^1n^2n^30$).

II. 4. 1. 1. «Quasi-spherical alkanes **QI** (code: n^1n^210).

QI subgroup includes five compounds, whose PMR spectra we have (**2210**, **3210**, **3310**, **4310**, **4410**). PMR spectrum of alkane **4210** absent.

2210 $\delta^H_{CH_3} = 0.845$ ppm [4], -30	3210 $\delta^H_{CH_3} = 0.788$ ppm [3], -90	3310 $\delta^H_{CH_3} = 0.737$ ppm [3], -140
4210 Data absent	4310 $\delta^H_{CH_3} = 0.745$ ppm [3], -130 , = 0.760 ppm [R], -120	4410 $\delta^H_{CH_3} = 0.860$ м.д. [7], -20

II. 4. 2. «Minimally spherical» compounds, **Min** (code: $n^1n^2n^31$).

II. 4. 2. 1. «Minimally spherical» I compounds, **MinI** (code: n^1n^211).

MinI subgroup includes five compounds, whose PMR spectra we have (**2211**, **4211**, **3311**, **4311**, **4411**). PMR spectrum of alkane **3211** absent.

2211 $\delta^H_{CH_3} = 0.797$ ppm [3], -80	3211 Data absent	4211 $\delta^H_{CH_3} = 0.770$ ppm [7], -110
3311 $\delta^H_{CH_3} = 0.681$ ppm [3], -200	4311 $\delta^H_{CH_3} = 0.760$ ppm [7], -120	4411 $\delta^H_{CH_3} = 0.830$ ppm [7], -50

II. 4. 2. 2. «Minimally spherical» I compounds, **MinII** (code: n^1n^221).

PMR spectra of 5 compounds are given: **2221**, **4221**, **4321**, **4331** and **4431**. PMR spectra of alkanes **3221**, **3321**, **3331**, **4421** and **4441** absent.

2221	3221	4221
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$\delta^{\text{H}}_{\text{CH}_3} = 0.742 \text{ ppm [3], -140}$

Data absent

 $\delta^{\text{H}}_{\text{CH}_3} = 0.730 \text{ ppm [7], -150}$ **3321**

Data absent

4321 $\delta^{\text{H}}_{\text{CH}_3} = 0.760 \text{ ppm [7], -120}$ **4421**

Data absent

3331

Data absent

4331 $\delta^{\text{H}}_{\text{CH}_3} = 0.770 \text{ ppm [7], -110}$ **4431** $\delta^{\text{H}}_{\text{CH}_3} = 0.830 \text{ ppm [7], -50}$ **4441**

Data absent

II. 5. The hydrogen atom H^3

The **hydrogen atom H^3** found in 22 of the 53 compounds under consideration. These compounds are: **2200, 2210, 2220, 3200, 3210, 3220, 3300, 3310, 3320, 3330, 4200, 4210, 4220, 4300, 4310, 4320, 4330, 4400, 4410, 4420, 4430, 4440**.

To emphasize the dominant presence of hydrogen atom the common code of these compounds, can be described as: $0\mathbf{n}^2\mathbf{n}^3\mathbf{n}^4$. We emphasize that such a designation does not correspond to the rules of precedence above substituents (as $\mathbf{n}^1 = 0 < 1, 2, 3, 4$).

At our disposal there are PMR spectral data for 20 of the possible 22 substances: **2200, 2210, 2220, 3200, 3210, 3220, 3300, 3310, 3320, 3330, 4200, 4220, 4300, 4310, 4320, 4400, 4410, 4420, 4430, 4440**. For two compounds - **4420** and **4430** - the signals of studied hydrogen atom not found by authors, so they are marked in bold italics. PMR spectra of 2 compounds: **4210, 4330** are absent for us.

All 22 possible alkanes we divide by the degree of their «sphericity».

Because of the structure peculiarities of the compounds in question are absent such groups of «spherical» alkanes as «**minimally spherical**» alkanes of two subgroups **MinI** and **MinII** as well as «**maximally spherical**» alkanes **Max**.

We have PMR spectra of all 6 «**quasi-linear**» alkanes (**L**): **2200, 3200, 3300, 4200, 4300, 4400**; 6 «**quasi-spherical**» alkanes of first subgroup (**QI**): **2210, 3210, 3310, 4210, 4310, 4410**; as well as 6 «**quasi-spherical**» alkanes of second subgroup (**QII**): **2220, 3220, 3320, 4220, 4320, 4420, 3330, 4330, 4430, 4440**.

II. 5. 1. «Quasi-linear» alkanes **L** (code: $\mathbf{n}^1\mathbf{n}^200$).

L group includes all six compounds, whose PMR spectra we have (**2200, 3200, 3300, 4200, 4300, 4400**).

2200 $\delta^{\text{H}}_{\text{CH}_3} = 1.260 \text{ ppm [3], -10}$ **3200** $\delta^{\text{H}}_{\text{CH}_3} = 1.150 \text{ ppm [3], -120}$ **4200** $\delta^{\text{H}}_{\text{CH}_3} = 1.150 \text{ ppm [4], -120}$ **3300** $\delta^{\text{H}}_{\text{H}} = 1.028 \text{ ppm [3], -240}$ **4300** $\delta^{\text{H}}_{\text{H}} = 1.122 \text{ ppm [3], -150}$ **4400** $\delta^{\text{H}}_{\text{H}} = 1.260 \text{ ppm [3], -10}$

II. 5. 2. «Quasi-spherical Q alkanes (code: n¹n²n³0).

II. 5. 2. 1. «Quasi-spherical alkanes QI (code: n¹n²10).

QI subgroup includes five of six possible compounds, whose PMR spectra we have (2210, 3210, 3310, 4310, 4410). PMR spectrum of alkane 4210 absent.

2210
 $\delta^{\text{H}}_{\text{CH}_3} = 1.240 \text{ ppm [4], -30}$

3210
 $\delta^{\text{H}}_{\text{CH}_3} = 1.170 \text{ ppm [3], -90}$

3310
 $\delta^{\text{H}}_{\text{CH}_3} = 0.970 \text{ ppm [3], -140}$

4210
 Data absent

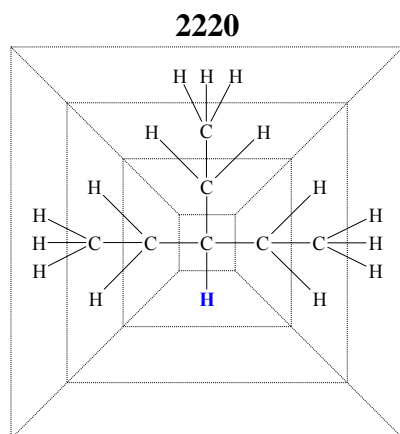
4310
 $\delta^{\text{H}}_{\text{CH}_3} = 1.137 \text{ ppm [3], -130,}$
 $= 1.150 \text{ ppm [7], -120}$

4410
 $\delta^{\text{H}}_{\text{CH}_3} = 1.180 \text{ м.д. [7], -20}$

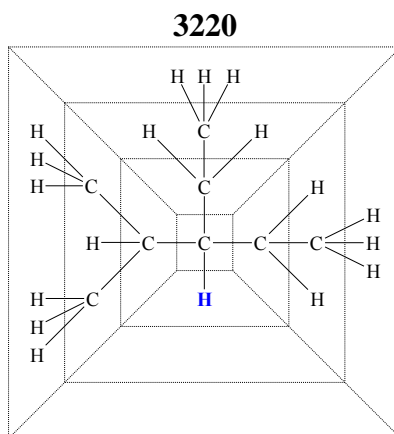
II. 5. 2. 2. «Quasi-spherical alkanes QII (code: n¹n²n³0).

QII subgroup includes five of six possible compounds, whose PMR spectra we have (2220, 3220, 4220, 3320, 4320, 4440). [In the spectrum of compound 4320 shown bracketed numeral, which is the arithmetic mean value of the interval, showing for the signals of two types of protons: methylene protons C²H² and signal C³H³ of discussed hydrogen atom]. PMR spectrum of alkanes 4330, 4420, 4430 absent. In two of them - 4420 and 4430 - in cited in [7] the studied spectra of the hydrogen atom signals were not found.

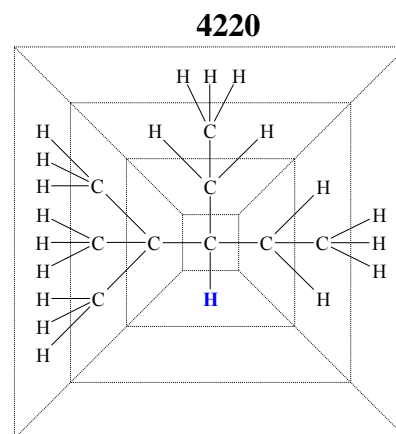
As mentioned above, for clarity, we give schematic representations of the ten quasi-spherical alkanes **QII** and values $\delta^{\text{H}}_{\text{H}}$ parameters of hydrogen atoms.



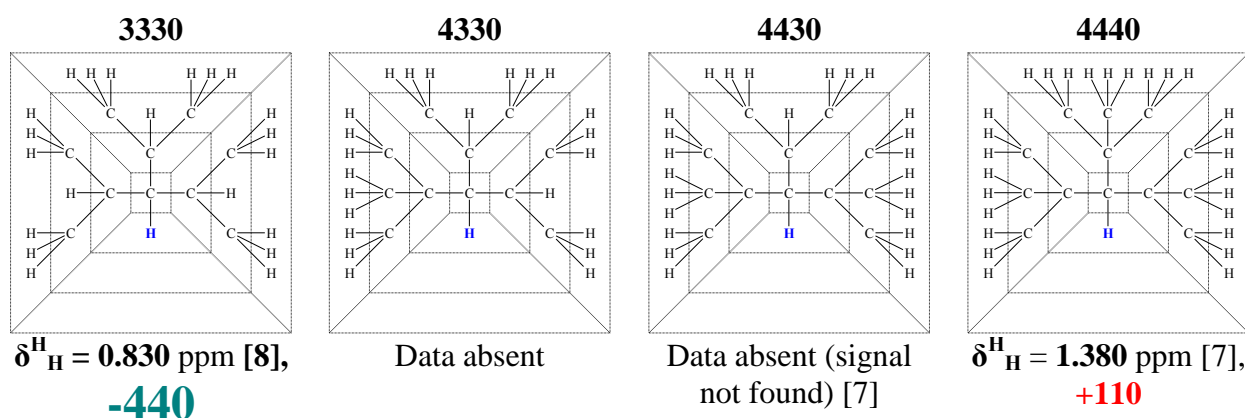
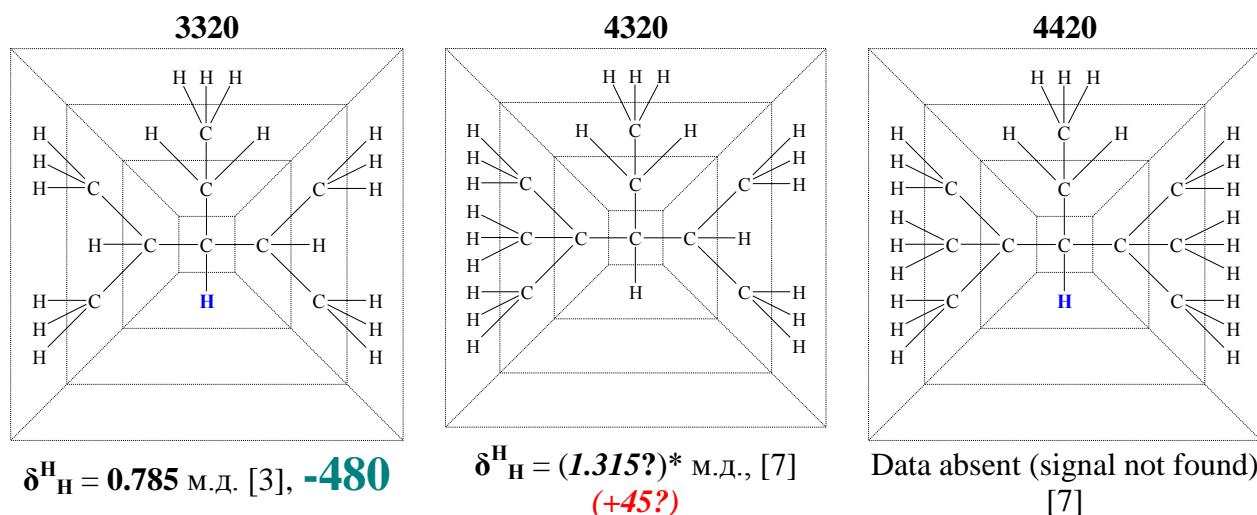
$\delta^{\text{H}}_{\text{H}} = 1.086 \text{ м.д. [3], -180}$



$\delta^{\text{H}}_{\text{H}} = 0.910 \text{ ppm [3], -360}$



$\delta^{\text{H}}_{\text{H}} = 0.733 \text{ ppm [3], -540}$



III. Discussion.

III. 1. Tabulating the $\Delta\delta^H$ values.

For clarity we reduce the values of the differential parameters $\Delta\delta^H$: $\Delta\delta^H_{\text{CH}_3}$, $\Delta\delta^H_{\text{CH}_2}$ and $\Delta\delta^H_{\text{CH}}$ for each of all 5 discussed fragments (branches) of every «ball-shaped alkane molecule» in Tables 1 - 7. Each compound is «placed» into the corresponding cell of the table accordingly the value of its geometric parameters:

- 1) **vertical** – from the number of hydrogen atoms **H** in the ω - layer, denoted by the symbol « H_ω »;
- 2) **horizontal**: a) from the degree of molecule «sphericity» estimated by the quantity of (2, 3 or 4) and «quality» (value **B** and / or *b*) carbonic branches.

The numerator specified number of the substance, and the denominator - the value of its differential parameter $\Delta\delta^H$, which includes the abovementioned method of image, color and font size.

As in the experimental part we begin our consideration of the **methyl groups** of long dicarbonic alkyl fragments **B** ($n^1, n^2 = 2, 3$ or **4**), hydrogen atoms of which are located in an **outer ω - layer**. In the Table 1 we consider the differential parameters $\Delta\delta^{\text{Et},\omega\text{-H}}_{\text{CH}_3}$ of ethyl group ($n^i = 2$), in the Table. 2 - $\Delta\delta^{\text{Pr},\omega\text{-H}}_{\text{CH}_3}$ parameters of isopropyl group ($n^i = 3$) and in the Table. 3 - $\Delta\delta^{\text{Bu}}_{\text{CH}_3}$ parameters of tert-butyl group ($n^i = 4$).

Then we consider the hydrogen atoms located in the **intermediate β - layer**: a) the parameters $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$ of two methylene hydrogen atoms of the ethyl group (Table 4); b) Parameters $\Delta\delta^{\text{Pr},\beta\text{-H}}_{\text{CH}}$

of one methyne hydrogen atom of the isopropyl group (Table 5); c) Parameters $\Delta\delta^{\text{Me},\beta\text{-H}}_{\text{CH}_3}$ of three methyl hydrogen atoms of short branches **b** (tab. 6).

Finally, we consider the parameters $\Delta\delta^{\text{H},\alpha\text{-H}}_{\text{CH}}$ of hydrogen atoms (H^3) which located in the **inner α -layer** (tab. 7).

Table 1.

The values of the differential parameters $\Delta\delta^{\text{Et},\omega\text{-H}}_{\text{CH}_3}$ of **ethyl** fragments in ethylcontaining «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_ω - The amount of hydrogen atoms in the outer layer (ω – layer)							
		6	9	12	15	15	18	21	24
«L»	2 (B+B)	<u>2200</u> 0	<u>3200</u> 0	<u>4200</u> 0					
«QI»	3 (B+B+b)	<u>2210</u> -20	<u>3210</u> -20	<u>4210</u> н.д.					
«QII»	3 (B+B+B)		<u>2220</u> -40	<u>3220</u> -20	<u>3320</u> +30	<u>4220</u> +40	<u>4320</u> +80	<u>4420</u> +90	
«Min I»	4 (B+B+b+b)	<u>2211</u> -90	<u>3211</u> н.д.	<u>4211</u> -50					
«Min II»	4 (B+B+B+b)		<u>2221</u> -120	<u>3221</u> н.д.	<u>4221</u> -50	<u>3321</u> н.д.	<u>4321</u> -10	<u>4421</u> н.д.	
«Max»	4 (B+B+B+B)			<u>2222</u> -150		<u>3222</u> н.д.	<u>4222</u> +30		<u>4422</u> +140

Table 2.

The values of the differential parameters $\Delta\delta^{\text{Pr},\omega\text{-H}}_{\text{CH}_3}$ of **isopropyl** fragments in isopropyl containing «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_ω - The amount of hydrogen atoms in the outer layer (ω – layer)						
		9	12	15	18	18	21	24
«L»	2 (B+B)	<u>3200</u> -20	<u>3300</u> -30	<u>4300</u> +30				
«QI»	3 (B+B+b)	<u>3210</u> -50	<u>3310</u> -40	<u>4310</u> -50				
«QII»	3 (B+B+B)		<u>3220</u> -50	<u>3320</u> -20	<u>3330</u> +50	<u>4320</u> -10	<u>4330</u> н.д.	<u>4430</u> +270
«Min I»	4 (B+B+b+b)	<u>3211</u> н.д.	<u>3311</u> -70	<u>4311</u> +10				
«Min II»	4 (B+B+B+b)		<u>3221</u> н.д.	<u>3321</u> н.д.	<u>3331</u> н.д.	<u>4321</u> +90	<u>4331</u> +130	<u>4431</u> +280
«Max»	4 (B+B+B+B)			<u>3222</u> н.д.	<u>3322</u> н.д.		<u>3332</u> н.д.	<u>4332</u> н.д.
	4 (B+B+B+B)						<u>4322</u> н.д.	<u>3333</u> н.д.

Table 3.

The values of the differential parameters $\Delta\delta^{\text{Bu}, \omega\text{-H}}_{\text{CH}_3}$ of **tert-butyl** fragments in tert-butyl containing «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_ω - The amount of hydrogen atoms in the outer layer (ω – layer)					
		12	15	18	21	24	27
«L»	2 (B+B)	<u>4200</u> -20	<u>4300</u> +10	<u>4400</u> +100			
«QI»	3 (B+B+b)	<u>4210</u> н.д.	<u>4310</u> -10	<u>4410</u> +100			
«QII»	3 (B+B+B)		<u>4220</u> -30	<u>4320</u> +10	<u>4420</u> +100	<u>4430</u> +270	<u>4440</u> +350
«Min I»	4 (B+B+b+b)	<u>4211</u> -20	<u>4311</u> +20	<u>4411</u> +110			
«Min II»	4 (B+B+B+b)		<u>4221</u> (-50?) -20	<u>4321</u> +50	<u>4331</u> +110	<u>4431</u> +200	<u>4441</u> н.д.
«Max»	4 (B+B+B+B)			<u>4222</u> +30	<u>4332</u> н.д.	<u>4422</u> +180	<u>4432</u> н.д.

Table 4.

The values of the differential parameters $\Delta\delta^{\text{Et}, \beta\text{-H}}_{\text{CH}_2}$ of **ethyl** fragments in ethylcontaining «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_ω - The amount of hydrogen atoms in the outer layer (ω – layer)							
		6	9	12	15	15	18	21	24
«L»	2 (B+B)	<u>2200</u> +30	<u>3200</u> +20	<u>4200</u> -20					
«QI»	3 (B+B+b)	<u>2210</u> -40	<u>3210</u> -40	<u>4210</u> н.д.					
«QII»	3 (B+B+B)		<u>2220</u> +10	<u>3220</u> -10	<u>3320</u> -20	<u>4220</u> +20	<u>4320</u> +50	<u>4420</u> +40	
«Min I»	4 (B+B+b+b)	<u>2211</u> -70	<u>3211</u> н.д.	<u>4211</u> +50					
«Min II»	4 (B+B+B+b)		<u>2221</u> -80	<u>3221</u> н.д.	<u>4221</u> +100	<u>3321</u> н.д.	<u>4321</u> +150	<u>4421</u> н.д.	
«Max»	4 (B+B+B+B)			<u>2222</u> -100		<u>3222</u> н.д.	<u>4222</u> +120		<u>4422</u> +300

Table 5.

The values of the differential parameters $\Delta\delta^{\text{Pr}, \beta\text{-H}}_{\text{CH}}$ of **isopropyl** fragments in isopropyl containing «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_{ω} - The amount of hydrogen atoms in the outer layer (ω – layer)						
		9	12	15	18	18	21	24
«L»	2 (B+B)	<u>3200</u> +270	<u>3300</u> +350	<u>4300</u> +390				
«QI»	3 (B+B+b)	<u>3210</u> +290	<u>3310</u> +370	<u>4310</u> +700				
«QII»	3 (B+B+B)		<u>3220</u> +420	<u>3320</u> +470	<u>3330</u> +620	<u>4320</u> +730	<u>4330</u> <u>н.д.</u>	<u>4430</u> +910
«Min I»	4 (B+B+b+b)	<u>3211</u> <u>н.д.</u>	<u>3311</u> +390	<u>4311</u> +540				
«Min II»	4 (B+B+B+b)		<u>3221</u> <u>н.д.</u>	<u>3321</u> <u>н.д.</u>	<u>3331</u> <u>н.д.</u>	<u>4321</u> +640	<u>4331</u> +740	<u>4431</u> +810
«Max» «L»	4 (B+B+B+B)			<u>3222</u> <u>н.д.</u>	<u>3322</u> <u>н.д.</u>		<u>3332</u> <u>н.д.</u>	<u>4332</u> <u>н.д.</u>
							<u>4322</u> <u>н.д.</u>	<u>3333</u> <u>н.д.</u>

Table 6.

The values of the differential parameters $\Delta\delta^{\text{Me}, \beta\text{-H}}_{\text{CH}_3}$ of **methyl** fragments in methyl containing «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_{ω} - The amount of hydrogen atoms in the outer layer (ω – layer)								
		6	9	12	12	15	18	21	24	27
«QI»	3 (B+B+b)	<u>221</u> <u>0</u> -30	<u>3210</u> -90	<u>3310</u> -140	<u>4210</u> <u>н.д.</u>	<u>4310</u> - 140?, -120?	<u>4410</u> -20			
«Min I»	4 (B+B+b+b)	<u>221</u> <u>1</u> -80	<u>3211</u> <u>н.д.</u>	<u>3311</u> - 200	<u>4211</u> -110	<u>4311</u> -120	<u>4411</u> -50			
«Min II»	4 (B+B+B+b)		<u>2221</u> -140	<u>3221</u> <u>н.д.</u>		<u>4221</u> -150	<u>4321</u> -120	<u>4331</u> -110	<u>4431</u> -50	<u>4441</u> <u>н.д.</u>
						<u>3321</u> <u>н.д.</u>	<u>3331</u> <u>н.д.</u>	<u>4421</u> <u>н.д.</u>		

Table 7.

The values of the differential parameters $\Delta\delta^{H,\alpha-H}_{CH}$ of **hydrogen atoms** from the **inner α -layer** in «spherical» alkanes.

molecule «sphericity»	The amount and constitution of C - branches	H_ω - The amount of hydrogen atoms in the outer layer (ω – layer)								
		6	9	12	12	15	18	21	24	27
«L»	2 (B+B)	<u>2200</u> -10	<u>3200</u> -120	<u>3300</u> -240	<u>4200</u> -120	<u>4300</u> -150	<u>4400</u> -10			
«QI»	3 (B+B+b)	<u>2210</u> -30	<u>3210</u> -100	<u>3310</u> -300	<u>4210</u> <u>H_Δ</u>	<u>4310</u> -130	<u>4410</u> -90			
«QII»	3 (B+B+B)		<u>2220</u> -180	<u>3220</u> -360		<u>4220</u> -540	<u>4320</u> (+45?)	<u>4330</u> <u>H_Δ</u>	<u>4430</u> <u>H_Δ</u>	<u>4440</u> +110
						<u>3320</u> -480	<u>3330</u> -440	<u>4420</u> <u>H_Δ</u>		

III. 2. Summary of Table 1 – 7 results.

Note that in each of the first four tables (1 - 4) the main part of the left side is «colored green», and the right - is «colored in the red». Therefore, they called, respectively, the «green zone» and «red zone». Sometimes we observed in these zones «the impregnations» of the opposite color. In Table 5, all the «squares» located in the **red zone**, but in tables 6 and 7 - almost all - in the green zone.

The most characteristic (called by us the term «**characterizing**») for each of the first four tables (1 - 4) in our opinion, are the spectral differential parameters of methyl (methylene) groups in an external (or intermediate) layer.

The first such parameter, we believe the greatest (by absolute magnitude) negative value of the parameter $\Delta\delta^{H}_{CH_3}$ ($\Delta\delta^{H}_{CH_2}$) of all other parameters listed in Tables 1 - 4 on lines that take into account this type of «sphericity» of the molecule. Of course, this parameter located in the «green zone». We denote him with the symbol «**H^{min}**». In Tables 8, 9, 11, 12 we give the values «**H^{min}**» and the value of parameter (**B + b**), defined for this type of «sphericity».

The second «characterizing» parameter we consider the so-called «**threshold of conversion**», which denoted as «**H^r**» symbol. The term «threshold of conversion» we mean the minimal amount of hydrogen atoms in the ω - layer, in which the differential parameter $\Delta\delta^{H}_{CH}$ ($\Delta\delta^{H}_{CH_3}$, $\Delta\delta^{H}_{CH_2}$, $\Delta\delta^{H}_{CH}$) exceeds the nominal value of the «average parameters», ie the value equal to **+50 mlrd.** Note that **H^r** parameter by definition locates in a «red zone», and is generally disposed near its left edge, slightly to the right of it.

We introduce new type of differential parameters, which characterized by parameters (**H^{min}** and **H^r**) of **methyl groups** which located in the outer layer. They designated as $\Delta\delta^{\omega-H}_{CH_3}$. These values are shown in Table 8; the values of **methylene groups** - in Table 9; the values of **methyne groups** – in Table 10; the values of **methyl groups**, which are located in the **intermediate β-layer** - in the table 11 and the values of hydrogen atoms from the **inner α-layer** - in Table 12.

Table 8

Characterizing parameters (H^{\min} and H_r) of methyl groups located in ω - layer.

The values of parameters:	Characterizing parameters $\Delta\delta^{\omega-H}_{CH_3}$ in alkanes with various types «sphericity»:																	
	«L» («00»)			«Q I» («10»)			«Q II» («20»)			«Min I» («11»)			«Min II» («21»)			«Max» («22»)		
	Et	Pr	Bu	Et	Pr	Bu	Et	Pr	Bu	Et	Pr	Bu	Et	Pr	Bu	Et	Pr	Bu
B + b	2+0	2+0	2+0	2+1	2+1	2+1	3+0	3+0	3+0	2+2	2+2	2+2	4	4	4	4	4	4
H_{\min} ($\Delta\delta^H$)	-	12	12	6,9	9	15	9	12	15	6	12	12	9	-?	15	12	-	-
H_r ($\Delta\delta^H$)	-	-	18	-	-	18	18	18	21	-	-	18	-	18	18	24?	-	24?
	-	-	+100	-	-	+100	+80	+50	+100	-	-	+100	-	+90	+50	+140?	-	+180?

Table 9

Characterizing parameters (H^{\min} and H_r) of methylene groups located in β - layer.

The values of parameters:	Characterizing parameters $\Delta\delta^{\beta-H}_{CH_2}$ in alkanes with various types «sphericity»:					
	«L» («00»)	«Q I» («10»)	«Q II» («20»)	«Min I» («11»)	«Min II» («21»)	«Max» («22»)
	Et	Et	Et	Et	Et	Et
B + b	2+0	2+1	3+0	2+2	3+1	4+0
H_{\min} ($\Delta\delta^H$)	12	6; 9	15	6	9	12
	-20	-40	-20	-70	-80	-100
H_r ($\Delta\delta^H$)	-	-	18	12	15	18
	-	-	+50	+50	+100	+120

Characterizing parameters (H_r) of methyne groups located in β - layer.

Above we have said, that we have no criterion for determining «the averaged value» of the chemical shift of methine protons in the middle of chain in the longchain linear alkanes ($\delta^{H,av}_{CH}$). This mean value should be similar to the afocited analogical values for methyl and methylene protons. However, this task is impossible because the **methyne hydrogen atoms in linear alkanes simply does not exist**. That's why we were forced to take as such criterion an averaged value of the chemical shift of mid methylene protons of longchain linear alkanes, equal to: $\delta^{H,av}_{CH_2} = 1.270$ ppm.

Table 5 shows that all values of considered parameters $\Delta\delta^{Pr,\beta-H}_{CH}$ are located in the «red zone»; moreover, they are equal to (or exceed) the number, equal to **+270 mlrd**. Therefore, a comparison of these parameters is not appropriate, and we have proposed a different path.

It was decided to accept as an alternative criterion («reduced the differential parameter») the **value of the base parameter δ^H_{CH} of isopropyl methine proton** the corresponding **parameter of simplest isopropylcontaining «spherical alkane» - 2-methylpentane (3200)**, the value of which is equal to **1.520** ppm. Then its «reduced the differential parameter» designated as $\Delta'\delta^H_{CH}$ will be equal to zero: $\Delta'\delta^H_{CH}^{3200} = 0$. The reduced the differential parameter $\Delta'\delta^H_{CH}$ calculated for other isopropylcontaining spherical alkanes make possible to calculate the «**reduced parameters H^r** », similar to parameters H^f . These parameters are included in Table 10 in place of lost meaning parameters H^{\min} .

Table 10

Reduced parameters H^r of methyne protons located in β -layer.

Parameter values	«Reduced parameters» $\Delta^r\delta^{\beta-H}_{CH}$ in the compounds with various types of «sphericity»:					
	«L» («00»)	«QI» («10»)	«QII» («20»)	«Min I» («11»)	«Min II» («21»)	«Max» («22»)
	Pr	Pr	Pr	Pr	Pr	Pr
$B + b$	2+0	2+1	3+0	2+2	3+1	4+0
H_r	9	9	12	12	18?	???
$(\Delta\delta^H)$	+270	+290	+420	+390	+640	???
H_r^r	12	9	12	12	18?	???
$(\Delta^r\delta^H)$	+80	+100	+150	+120	+390	???

Table 11

Characterizing parameters (H^{\min} and H^r) of methyl groups located in β - layer.

Parameter values	Characterizing parameters $\Delta\delta^{\beta-H}_{CH_3}$ in the compounds with various types of «sphericity»:		
	«QI» («10»)	«Min I» («11»)	«Min II» («21»)
	CH ₃	CH ₃	CH ₃
b	3	4	4
H_{\min}	12; 15	12	15
$(\Delta\delta^H)$	-140	-200	-150
H_r	-	-	-
$(\Delta\delta^H)$	-	-	-

Table 12

Characterizing parameters (H^{\min} and H^r) of hydrogen atoms \underline{H} -C³, located in α -layer.

Parameter values	Характеризующие параметры $\Delta\delta^{\alpha-H}_{CH}$ in the compounds with various types of «sphericity»:		
	«L» («00»)	«QI» («10»)	«QII» («20»)
	H	H	H
b	2	3	3
H_{\min}	12	12	15
$(\Delta\delta^H)$	-240	-300	-540
H_r	-	-	27
$(\Delta\delta^H)$	-	-	+110

Let us sum subtotals. Extremal characterizing parameters H^{\min} and H^r depending on the «sphericity» type alkanes are equal to:

1) $\Delta\delta^{Et,\omega-H}_{CH_3}$ in Et- containing alkanes are: $H^{\min} = \Delta\delta^{2222}_H = -150$ mlrd. (Max; $H_{\omega} = 12$); $H^r = \Delta\delta^{4320}_H = +80$ mlrd. (QII; $H_{\omega} = 18$).

- 2) $\Delta\delta^{\text{Pr},\omega\text{-H}}_{\text{CH}_3}$ in **Pr**- containing alkanes are: $\mathbf{H}^{\text{min}} = \Delta\delta^{3311}_{\text{H}} = -70$ mlrd. (**Min I**; $\mathbf{H}_\omega = 12$); $\mathbf{H}^{\text{r}} = \Delta\delta^{3330}_{\text{H}} = +50$ mlrd. (**Min II**; $\mathbf{H}_\omega = 18$).
- 3) $\Delta\delta^{\text{Bu},\omega\text{-H}}_{\text{CH}_3}$ in **Bu**- containing alkanes are: $\mathbf{H}^{\text{min}} = \Delta\delta^{4220}_{\text{H}} = -30$ mlrd. (**QII**; $\mathbf{H}_\omega = 15$); $\mathbf{H}^{\text{r}} = \Delta\delta^{4321}_{\text{H}} = +50$ mlrd. (**Min II**; $\mathbf{H}_\omega = 18$).
- 4) $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$ in **Et**- containing alkanes are: $\mathbf{H}^{\text{min}} = \Delta\delta^{2222}_{\text{H}} = -100$ mlrd. (**Max**; $\mathbf{H}_\omega = 12$); $\mathbf{H}^{\text{r}} = \Delta\delta^{4221}_{\text{H}} = +100$ mlrd. (**Min II**; $\mathbf{H}_\omega = 15$).
- 5) $\Delta\delta^{\text{Pr},\beta\text{-H}}_{\text{CH}}$ in **Pr**- containing alkanes are: $\mathbf{H}^{\text{r}} = \Delta\delta^{3310}_{\text{H}} = +100$ mlrd. (**QI**; $\mathbf{H}_\omega = 12$).
- 6) $\Delta\delta^{\text{Me},\beta\text{-H}}_{\text{CH}_3}$ in **Me**- containing alkanes are: $\mathbf{H}^{\text{min}} = \Delta\delta^{3311}_{\text{H}} = -200$ mlrd. (**Min I**; $\mathbf{H}_\omega = 12$); $\mathbf{H}^{\text{r}} = \text{absent}$.
- 7) $\Delta\delta^{\text{H},\alpha\text{-H}}_{\text{H}}$ in **H³**- containing alkanes are: $\mathbf{H}^{\text{min}} = \Delta\delta^{4220}_{\text{H}} = -540$ mlrd. (**QII**; $\mathbf{H}_\omega = 15$); $\mathbf{H}^{\text{r}} = \Delta\delta^{4440}_{\text{H}} = +100$ mlrd. (**QII**; $\mathbf{H}_\omega = 27$).

Extremal characterizing **parameters \mathbf{H}^{min}** for six of seven above types of protons (except parameter $\Delta\delta^{\text{Pr},\beta\text{-H}}_{\text{CH}}$) **achieved at values $\mathbf{H}_\omega = 12$ or $\mathbf{H}_\omega = 15$** . Compounds, for which these parameters \mathbf{H}^{min} obtained, usually have the **highest possible degree of sphericity**.

Considering the incompleteness of spectral data at our disposal, the conclusions obtained by us are only approximate and may be changed when new important data will be obtained. In particular, it relates to an isopropyl moiety (for which there is no chief data not only for compound **Min II – 3221**, but also to compound **Max – 3222**, where $\mathbf{H}_\omega = 15$) and to t-butyl moiety (where absent the essential data for compound **QI – 4210**, $\mathbf{H}_\omega = 12$).

III. 3. The search of dependences of differential spectral parameters $\Delta\delta^{\text{H}}$ ($\Delta\delta^{\text{H}}_{\text{CH}_3}$, $\Delta\delta^{\text{H}}_{\text{CH}_2}$ and $\Delta\delta^{\text{H}}_{\text{CH}}$) on the geometric peculiarities of alkane «spherical molecules».

The above shows that the differential spectral parameters $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ and $\Delta\delta^{\beta\text{-H}}_{\text{CH}_2}$ can be either positive or negative, whereas the parameters of methyne groups $\Delta\delta^{\beta\text{-H}}_{\text{CH}}$ of **β -layer** have exclusively positive value, and the parameters $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ also of **β -layer**, discussed in table 6, and the parameters of the $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ of **α -layer** examined in table 7, are almost exclusively negative. This different distribution of differential spectral parameters $\Delta\delta^{\text{H}}$ by the sign leads to the necessity for their separate discussion.

Note that the series of molecules with the same «sphericity» for ethyl, isopropyl and tert-butyl fragments it is advisable to be divided into two types depending on the ratios in these parameters **B** and **b**, i.e., on short and long.

Each of the three «**short**» series, existing for the **B**-branches (**Et**, **Pr**, **Bu**), namely: a) quasi-linear **L** («**00**»), b) «quasi-spherical » **QI** («**10**») and c) «minimally spherical » **Min I** (**11**) types of molecules comprises three compounds. In this short series the maximum possible values \mathbf{H}_ω , are follows: **12** for the ethyl, **15** for isopropyl and **18** for t-butyl fragments.

The remaining three types of spherical molecules: «quasi-spherical» **QII** («**20**»), the «minimally spherical» **Min II** (**21**) and the «maximally spherical» **Max** (**22**) form a «**long**» series with the number of compounds over three (typically 6 or 10)

For methyl group (located in the intermediate **β - layer**) and hydrogen atoms of inner **α - layer** «short» series absent at all. And quasi-linear» **L**, «quasi-spherical» **QI** and «minimally spherical» **Min I** types of molecules form the «long» series», each consisting of six compounds.

Obviously, in the short series, it is difficult to trace the subtle change of stadiing dependences $\Delta\delta^{\text{H}}$ on \mathbf{H}_ω . This can be done only in long series.

III. 3. 1. The dependence of $\Delta\delta^{\text{H}}_{\text{CH}_3}$ values of methyl groups, located in an external ω – layer and $\Delta\delta^{\text{H}}_{\text{CH}_2}$ values of methylene groups, located in the intermediate β - layer, on the values of the structural parameters B (b) and H_{ω} .

Let us see how the values of parameters $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ of Et, Pr and Bu- fragments (or $\Delta\delta^{\beta\text{-H}}_{\text{CH}_2}$ of Et fragments) changes in the «long» series with increasing of H_{ω} -values. Examination of the data in Tables 1 - 4 show similar trends of these changes to all three of these fragments: ethyl ($\Delta\delta^{\text{Et},\omega\text{-H}}_{\text{CH}_3}$, and $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$), isopropyl ($\Delta\delta^{\text{Pr},\omega\text{-H}}_{\text{CH}_3}$) and tert-butyl ($\Delta\delta^{\text{Bu},\omega\text{-H}}_{\text{CH}_3}$). In almost all cases (ie, for all three versions of alkane molecules «sphericity» that give a long series) the **changes of $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ and $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$ values with increasing of H_{ω} values going the same way.** The **most negative** value (ie, the largest in absolute value) of parameter $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ (or $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$) found with a minimum value of the parameter H_{ω} . With increasing of the parameter H_{ω} parameter $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ (or $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$) **starts to gradually increase, crossing in a positive value**, which at the further growth of H_{ω} -values **continues to increase**. Just for this reason, the above described parameters, characterizing the methyl groups (H_{min} and H_{r}) were selected.

Let us note that the values H_{min} , shown in Table 8 for a long series, generally amount or 9, or 12, or 15 hydrogen atoms .

If to considering of the long series we add the considering of short series, it becomes obvious that the greatest absolute magnitude negative value H_{min} of $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ parameters, among all three types of B-branches (Et, Pr, Bu) are found for ethyl fragments ($\Delta\delta^{\text{Et},\omega\text{-H}}_{\text{CH}_3}$), and exactly at the initial members of rows: 11, 21 and 22, respectively; i.e., at compounds 2211 ($\Delta\delta^{2211}_{\text{CH}_3}$), 2221 ($\Delta\delta^{2221}_{\text{CH}_3}$) and 2222 ($\Delta\delta^{2222}_{\text{CH}_3}$). Also the greatest absolute magnitude negative value H_{min} of $\Delta\delta^{\text{Et},\beta\text{-H}}_{\text{CH}_2}$ parameters are the parameters of the same compounds 2211, 2221 and 2222, respectively: ($\Delta\delta^{2211}_{\text{CH}_2}$), ($\Delta\delta^{2221}_{\text{CH}_2}$), and ($\Delta\delta^{2222}_{\text{CH}_2}$).

Regarding H_{r} parameter it is more difficult to express a definite opinion due to lack of data for the long series of «maximally spherical» molecules Max (22), since there are no data for the «key» values H_{ω} , namely for 18 and 21 hydrogen atoms. However, the magnitude of the «threshold of conversion», (H_{r}) for two other series are identical and both equal to 18 hydrogen atoms.

III. 3. 2. The dependence of $\Delta\delta^{\text{H}}_{\text{CH}_3}$ values of methyl groups, located in the intermediate β - layer, on the values of the structural parameters B (b) and H_{ω} .

Let us see what changes of the parameter $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ values of Me-fragment occur in three now the «long» series of compounds **QI**, **Min I** and **Max** with increasing of H_{ω} -values.

Examination of the data in Table 6 shows that the $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ values passes through a minimum, which is situated in the area of $H_{\omega} = 12 - 15$ (see Table 11). This means that the negative of the sign value, which have parameters $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ when values H_{ω} are minimal (eg, $H_{\omega} = 6$ or 9), with the growth of parameter H_{ω} firstly becomes more «negative» (ie, increases its absolute value), reaching a minimum (referred to as H_{min}). This minimum locates in the area of H_{ω} values equal to 12 or 15. Then, with growing H_{ω} values, since $H_{\omega} = 18$, the parameters $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ become more «positive» (ie, they decreases by magnitude of the absolute negative value), while remaining the negative sign. Positive values of the $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ parameters were not observed, probably due to our lack of data for compounds with a sufficiently large H_{ω} values (eg, $H_{\omega} = 21$ for a series of **QI** or **Min I**, or $H_{\omega} = 27$ for serie **Max**).

III. 3. 3. The dependence of $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ values of hydrogen atoms, located in the inner α - layer, on the values of the structural parameters B (b) and H_{ω} .

Let us now see what changes of the parameters $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ of $\text{H}^3\text{-C}^3$ hydrogen atoms occur in three is now «long» series of compounds (**L**, **QI**, and **QII**) with increasing the parameter H_{ω} value.

Examination of the data in Table 7 shows that the parameter $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ value, as the one discussed above in section III. 3. 2. $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$ magnitude, **passes through a minimum**, which is also situated **in the area** of values $H_{\omega} = 12 - 15$ (see Table 12).

But, unlike the parameter $\Delta\delta^{\beta\text{-H}}_{\text{CH}_3}$, for parameter $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ noted also the **presence of his positive values** ($\Delta\delta^{\alpha\text{-H}}_{\text{H}} = +110$ mlrd.) for sufficiently large values $H_{\omega} = 27$ in **QII** serie. At the same time the **positive values** of parameter $\Delta\delta^{\alpha\text{-H}}_{\text{H}}$ **were not observed** for two other series: **L** and **QI**. Perhaps this is due to lack of compounds with large enough values parameter $H_{\omega} = 21$, which in this series do not exist by definition.

III. 3. 4. The generalization of the conclusions of Sections III.3.1. - III.3.3.

Putting together what said in Section III. 3. 1. - III. 3. 3., we note the following:

- **There is an identity (or strong similarity) in the behavior of all four** discussed fragments [a) CH_3 in **B** branches; b) CH_2 in **Et**, c) CH_3 in **b** branches; and d) **H** in $\text{C}^3\text{-H}^3$ fragment] **with respect to changes in the magnitude of $\Delta\delta^{\omega\text{-H}}_{\text{CH}_3}$ parameter (or $\Delta\delta^{\beta\text{-H}}_{\text{CH}_2}$) with increasing the parameter H_{ω} value.** In all cases, **starting with a certain H_{ω} value** ($H_{\omega} = 12$), the **increasing the number of hydrogen atoms** in the ω - layer **leads to an increase in the value of the $\Delta\delta^{\text{H}}$ parameter.** In the case of two fragments of molecule that are not located in the outer layer: [c) CH_3 in branches **b** and d) **H** in $\text{C}^3\text{-H}^3$] during the **growth** of H_{ω} from the smallest value ($H_{\omega} = 6, 9$) to the «mid» values ($H_{\omega} = 12$) we observed in first a **decreasing of $\Delta\delta^{\text{H}}$ parameter values** before reaching its **minimal value** (H_{min}), and only after that the abovementioned **growth**.

Let us note also that the **increase** of the parameter $\Delta\delta^{\text{H}}_{\text{CH}}$ value for **methyne protons** (**CH** in **Pr**) with an **increase in the value of the parameter H_{ω}** also observed in all five rows, presented in Table 3 for the methyne protons of isopropyl group, for which we have data PMR. The difference with the abovementioned other four fragments: [a) CH_3 in **B** branches; b) CH_2 in **Et**; c) CH_3 in **b** branches; and d) **H** in $\text{C}^3\text{-H}^3$ fragment] that **all parameters $\Delta\delta^{\text{H}}_{\text{CH}}$ for the methyne protons (CH in Pr) shown in table 5, starting with the lowest values of the parameters H_{ω} ($H_{\omega} = 6$) have positive values.**

III. 4. The searching of differential parameters $\Delta\delta^{\text{H}}$ dependences from the distribution uniformity of hydrogen atoms in the outer ω - layer.

In this last section of the resulting discussion we shall take an effort to find the **dependences of differential parameters $\Delta\delta^{\text{H}}$ values on the uniformity of hydrogen atoms in the outer ω - layer distribution.** For this we consider the peculiarities of the distribution of hydrogen atoms in the volume of ω - layer in some ethyl- and t-butylcontaining spherical alkanes. Due to lack of available spectral data for isopropylcontaining spherical alkanes we consider them only in some aspects.

III. 4. 1. The comparison of differential parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ and $\Delta\delta^{\text{H}}_{\text{CH}_2}$ values of ethylcontaining spherical alkanes' ethyl fragments.

III. 4. 1. 1. The comparison of parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ and $\Delta\delta^{\text{H}}_{\text{CH}_2}$ of ethyl fragments during the transition from «quasi-linear» 2200 to «maximally spherical» 2222 alkanes: (2200 \rightarrow \rightarrow 2222).

Let us consider the change of the differential parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ and $\Delta\delta^{\text{H}}_{\text{CH}_2}$ in a row, where the transition from a simple quasi-linear alkane (2200) to the most complex of all alkanes, in which only ethyl groups occur as long branches (**B**) - the maximally spherical alkane - 2222. There are six such compounds in this row (including the initial and final substances): 2200, 2210, 2211, 2220, 2221 and 2222.

Let us consider two possible ways of this transition. For this, we give for each stage in these processes the values of the differential parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ and $\Delta\delta^{\text{H}}_{\text{CH}_2}$ for final and initial substance of such stage, as well as their difference, designated, respectively, as $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3}$ and $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2}$.

The first («slow») four -step path can be considered as the most «gradual». It involves the gradual replacement of both hydrogen atoms from the inner α -layer (the third and fourth branch in compound 2200) on the methyl groups, (H-atoms of which are not in the inner α -layer, but in the intermediate β - layer). Then followed by gradual replacement of both of these methyl groups to ethyl groups (CH_3 -atoms of which are already in the outer ω -layer). This way described by the scheme: 2200 \rightarrow 2210 \rightarrow 2211 \rightarrow 2221 \rightarrow 2222. We consider separately the methyl and methylene fragments of ethyl group.

Methyl fragment.

The first stage. 2200 (0) \rightarrow 2210 (-20) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-20)$.

The second stage. 2210 (-20) \rightarrow 2211 (-90) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-70)$.

The first plus second stage. 2200 (0) \rightarrow 2211 (-90) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-90)$.

The third stage. 2211 (-90) \rightarrow 2221 (-120) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-30)$.

The fourth stage. 2221 (-120) \rightarrow 2222 (-150) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-30)$.

Methylene fragment.

The first stage. 2200 (+30) \rightarrow 2210 (-40) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-70)$.

The second stage. 2210 (-40) \rightarrow 2211 (-70) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-30)$.

The first plus second stage. 2200 (+30) \rightarrow 2211 (-70) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-100)$.

The third stage. 2211 (-70) \rightarrow 2221 (-80) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-10)$.

The fourth stage. 2221 (-80) \rightarrow 2222 (-100) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-20)$.

The second («fast») two-step path includes the gradual replacement of the hydrogen atoms of the inner α -layer (the third and fourth branches of the compound 2200) directly to the «final» ethyl group, and looks like this: : 2200 \rightarrow 2220 \rightarrow 2222.

Methyl fragment.

The first stage. 2200 (0) \rightarrow 2220 (-40) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-40)$.

The second stage. 2220 (-40) \rightarrow 2222 (-150) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-110)$.

Methylene fragment.

The first stage. . 2200 (+30) \rightarrow 2220 (+10) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-20)$.

The second stage. 2220 (+10) \rightarrow 2222 (-100) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_2} = (-120)$.

Let us comment on the above data.

1. Let us note the almost complete similarity in the behavior of both differential parameters ($\Delta\delta_{\text{CH}_3}^{\text{H}}$ and $\Delta\delta_{\text{CH}_2}^{\text{H}}$) in both ways of the aforementioned transition: **2200** \rightarrow **2222**.

2. We emphasize that all the differences (both $\Delta\delta_{\text{CH}_3}^{\text{H}}$ and $\Delta\delta_{\text{CH}_2}^{\text{H}}$) in each stage both four -step and two-step transitions are negative values. Their magnitudes range from **-10** to **-120** mlrd.

III. 4. 2. The comparison of the differential parameter $\Delta\delta_{\text{CH}_3}^{\text{H}}$ values of tert-butyl fragments in tert-butylcontaining spherical alkanes.

III. 4. 2. 1. The comparison of parameters $\Delta\delta_{\text{CH}_3}^{\text{H}}$ values of tert-butyl fragments in transition from quasi-linear (4400) to quasi-spherical II alkane 4440: (4400 \rightarrow \rightarrow 4440).

Since at our disposal are no spectral data for compound **4444**, we have to limit ourselves during the consideration of «gradual» way only the first part of it, namely, the transition **4400** \rightarrow \rightarrow **4440**. Naturally, the review of the two-stage way at the same time does not make sense.

As for the above-considered «slow» transition **2200** \rightarrow \rightarrow **2222**, let us consider firstly for transition **4400** \rightarrow \rightarrow **4440** the longest «slow» ten-step path, including all the possible intermediates: **4400** \rightarrow **4410** \rightarrow **4411** \rightarrow **4420** \rightarrow **4421** \rightarrow **4422** \rightarrow **4430** \rightarrow **4431** \rightarrow **4432** \rightarrow **4433** \rightarrow **4440**. Unfortunately, since there is no spectral data of the compounds **4421**, **4422**, and **4433**, the ten-step path is reduced to seven-step path: **4400** \rightarrow **4410** \rightarrow **4411** \rightarrow **4420** \rightarrow **4422** \rightarrow **4430** \rightarrow **4431** \rightarrow **4440**.

It is possible that the inclusion of all 9 intermediates in the ten-step path is redundant, since the transitions **4411** \rightarrow **4420** and **4422** \rightarrow **4430** are logically to consider as a return from the more branched to the less branched compounds, which is impractical. So instead of seven-step path let us look the five-step path: **4400** \rightarrow **4410** \rightarrow **4411** \rightarrow **4422** \rightarrow **4440**, that is the part of the full seven-step path: **4400** \rightarrow **4410** \rightarrow **4411** \rightarrow [4421] \rightarrow **4422** \rightarrow {4432} \rightarrow [4433] \rightarrow **4440**. However, in this five-step path still has a logical defect. Instead of the absent spectrum of the expected compound **4432**, we forced to use less logically reasonable compound **4431**, the spectrum of which we have.

Five-step path.

The first stage. **4400 (+100)** \rightarrow **4410 (+100)**: $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}} = (0)$.

The second stage. **4410 (+100)** \rightarrow **4411 (+110)**: $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}} = (+10)$.

The third stage. **4411 (+110)** \rightarrow **4422 (+180)**: $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}} = (+70)$.

The fourth stage. **4422 (+180)** \rightarrow {**4431**} **(+200)**: $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}} = (+20)$.

The fifth stage. {**4431**} **(+200)** \rightarrow **4440 (+350)**: $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}} = (+150)$.

Let us comment on the above data.

1. Note that in contrast to the above transition **2200** \rightarrow **2222**, where each parameter $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}}$ is negative numeric, all the differences $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}}$ in each stage of five-step transition **4400** \rightarrow \rightarrow **4440** are either or zero, or positive values. Their values range from **+10** to **+150** mlrd.

2. Interestingly, that for two first stages the parameters $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}}$ are practically zero values. And for the last two stages (third and also fourth plus fifth) $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}}$ parameters are fairly large positive values (from **+70** to **+85** mlrd.).

III. 4. 3. The comparison of the differential parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ values of ethyl- and of tert-butyl- fragments in ethyltert-butyl containing spherical alkanes.

III. 4. 3. 1. The comparison of differential parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ of **ethyl-** and of **tert-butyl-** fragments in transition from quasi-linear (4200) to «maximally spherical» alkane 4222: (4200 \rightarrow \rightarrow 4222).

Now let us consider the transition 4200 \rightarrow \rightarrow 4222, wherein all the compounds include contemporaneously both ethyl, and t-butyl groups. This transition (among other possible) was chosen because for all (except one) compounds we have the spectral data at our disposal.

To transition 4200 \rightarrow \rightarrow 4222 also two ways are possible. The first (slow) way is four-stage path: 4200 \rightarrow [4210] \rightarrow 4211 \rightarrow 4221 \rightarrow 4222. But since there is no data for compound 4210, this four-stage path is reduced to three-stage one by replacing of the first and second stages on the first plus second path: 4200 \rightarrow 4211 \rightarrow 4221 \rightarrow 4222. The second way – is two-stage path: 4200 \rightarrow 4220 \rightarrow 4222.

III. 4. 3. 1. 1. The comparison of parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ values of **tert-butyl-** fragments in ethyltert-butyl containing spherical alkanes in transition 4200 \rightarrow \rightarrow 4222.

Three-stage path.

The first plus second stage. 4200 (-20) \rightarrow 4211 (-20): $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (0)$.

The third stage. 4211 (-20) \rightarrow 4221 (-20): $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (0)$.

The fourth stage. 4221 (-20) \rightarrow 4222 (+30) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (+50)$.

The two-stage path.

The first stage. . 4200 (-20) \rightarrow 4220 (-30): $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (-30)$.

The second stage. 4220 (-30) \rightarrow 4222 (+30) : $\Delta\Delta\delta^{\text{H}}_{\text{CH}_3} = (+60)$.

Let us comment on the above data.

1. In the three-stage path the first two stages have zero value, and a third stage – the positive value. This demonstrates similarities with the behavior of t-butyl fragment in the five-step transition discussed above: 4400 \rightarrow \rightarrow 4440.

2. The comparison of the two-step transition path: 4200 \rightarrow \rightarrow 4222 with the two-step transition path: 4400 \rightarrow \rightarrow 4444, is impossible, since the latter the second stage: 4440 \rightarrow \rightarrow 4444 is absent.

III. 4. 3. 1. 2. The comparison of parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ values of **ethyl-** fragments in ethyltert-butyl containing spherical alkanes in transition 4200 \rightarrow \rightarrow 4222.

Methyl fragment.

Let us consider again the transition 4200 \rightarrow \rightarrow 4222, where are possible two ways: three-stage path: 4200 \rightarrow 4211 \rightarrow 4221 \rightarrow 4222 and a two-stage path: 4200 \rightarrow 4220 \rightarrow 4222.

Three-stage path.

The first plus second stage. $4200 (0) \rightarrow 4211 (-50) : \underline{\Delta\Delta\delta^H_{CH_3}} = (-50)$.

The third stage. $4211 (-50) \rightarrow 4221 (-50) : \underline{\Delta\Delta\delta^H_{CH_3}} = (0)$.

The fourth stage. $4221 (-50) \rightarrow 4222 (+30) : \underline{\Delta\Delta\delta^H_{CH_3}} = (+80)$.

The two-stage path..

The first stage. $4200 (0) \rightarrow 4220 (+40) : \underline{\Delta\Delta\delta^H_{CH_3}} = (+40)$.

The second stage. $4220 (+40) \rightarrow 4222 (+30) : \underline{\Delta\Delta\delta^H_{CH_3}} = (-10)$.

Let us comment on the above data.

1. Note that the reporting three-stage way **fundamentally different** from the considered above four-stage way in transition $2200 \rightarrow 2222$ (where each parameter $\underline{\Delta\Delta\delta^H_{CH_3}}$ is a **negative** number). **The difference is that** in three-stage path in the first stage the parameter $\underline{\Delta\Delta\delta^H_{CH_3}}$ is a **negative** number; in the second stage – this parameter is **zero number**, and in the third stage it is a **positive** numeric.

2. The two-step transition path $4200 \rightarrow \rightarrow 4222$ is **fundamentally different** from the two-step transition path $2200 \rightarrow 2222$ also, as the **first stage** in it is **opposite by sign to the first stage** of transition $2200 \rightarrow 2222$. The **last stage** in both transitions are **negative by sign**. But in absolute value in transition path $4200 \rightarrow 4222$ it is an order of magnitude lower than the corresponding value in the last stage of transition $2200 \rightarrow 2222$.

The first stage. $2200 (+30) \rightarrow 2220 (+10) : \underline{\Delta\Delta\delta^H_{CH_2}} = (-20)$.

The second stage. $2220 (+10) \rightarrow 2222 (-100) : \underline{\Delta\Delta\delta^H_{CH_2}} = (-120)$.

III. 4. 3. 1. 3. The comparison of differential parameter $\Delta\delta^H_{CH_2}$ values of **ethyl-** fragment of methylene groups in ethyltert-butyl containing spherical alkanes in transition $4200 \rightarrow \rightarrow 4222$.

Three-stage path.

The first plus second stage. $4200 (-20) \rightarrow 4211 (+50) : \underline{\Delta\Delta\delta^H_{CH_2}} = (+70)$.

The third stage. $4211 (+50) \rightarrow 4221 (+100) : \underline{\Delta\Delta\delta^H_{CH_2}} = (+50)$.

The fourth stage. $4221 (+100) \rightarrow 4222 (+110) : \underline{\Delta\Delta\delta^H_{CH_2}} = (+10)$.

The two-step way.

The first stage. $4200 (-20) \rightarrow 4220 (+20) : \underline{\Delta\Delta\delta^H_{CH_2}} = (+40)$.

The second stage. $4220 (+20) \rightarrow 4222 (+110) : \underline{\Delta\Delta\delta^H_{CH_2}} = (+90)$.

Let us comment on the above data.

1. All three parameters $\underline{\Delta\Delta\delta^H_{CH_2}}$ in both types of transition $4200 \rightarrow \rightarrow 4222$ are **positive** values, whereas the same parameters in both transitions $2200 \rightarrow \rightarrow 2222$ are **negative numeric**.

2. For three-stage way in transition $4200 \rightarrow \rightarrow 4222$ we see a **gradual reduction** of the **positive** value of the parameter $\underline{\Delta\Delta\delta^H_{CH_2}}$ ($+70 \rightarrow +50 \rightarrow +10$).

3. For methylene group the change of differential parameters $\Delta\delta^H_{CH_2}$ in transition $4200 \rightarrow \rightarrow 4222$ **very much different** from the one discussed above differential parameters change $\Delta\delta^H_{CH_3}$.

4. For three-stage path we observed the abovenoted **decrease** of **positive** values of **methylene** group parameter $\Delta\Delta\delta_{\text{CH}_2}^{\text{H}}$ (**+70** \rightarrow **+50** \rightarrow **+10**), in contrast to the abovementioned **gradual** and rather steep increase of positive value of the **methyl** group parameter $\Delta\Delta\delta_{\text{CH}_3}^{\text{H}}$ (**-50** \rightarrow **0** \rightarrow **+80**).

III. 4. 3. 2. The preliminary conclusion on the section III. 4. 3. 1.

The replacing of ethyl group on tert-butyl group in the considered above pair of transitions results in a **fundamentally different behavior** of both differential parameters $\Delta\delta_{\text{CH}_3}^{\text{H}}$ and $\Delta\delta_{\text{CH}_2}^{\text{H}}$. Therefore it seems appropriate to consider our understanding of the reasons for such the different behavior of the two fragments of an ethyl group (methyl and methylene), depending on the remaining branches of the spherical molecule.

III. 5. Our conception of the relationship between structure of ethyl, isopropyl and tert-butylcontaining spherical alkanes and differential spectral parameters $\Delta\delta_{\text{CH}_3}^{\text{H}}$ and $\Delta\delta_{\text{CH}_2}^{\text{H}}$ values of **ethyl, isopropyl and tert-butyl** fragments in them.

We offer our vision of the relationship between structure of ethyl, isopropyl and tert-butylcontaining spherical alkanes and differential spectral parameters $\Delta\delta_{\text{CH}_3}^{\text{H}}$ and $\Delta\delta_{\text{CH}_2}^{\text{H}}$ values in this fragments. Let's start with the description of simplest structure of «completely» tert-butylcontaining spherical alkanes (as we consider only the hydrogen atoms of the methyl groups which located in the outer layer, ie. $\Delta\delta_{\text{CH}_3}^{\text{H}}$ parameters). So we starting with a «quasi-linear» compound **4400**.

III. 5. 1. The relationship of tert-butylcontaining spherical alkanes structure and differential spectral parameters $\Delta\delta_{\text{CH}_3}^{\text{H}}$ of **tert-butyl** fragments in «quasi-linear» compound **4400**.

Let us consider the structure of the simplest tert-butylcontaining compound - di-tert-butylmethane (2,2,4,4-tetramethylpentane), designated by us as **4400**. According to the definition given above this is a **quasi-linear** alkane, since there is no branching exactly in the central atom C^3 in it.

Although formally the molecule **4400** regarded as linear one, in fact the angle $\text{C}^2\text{-C}^3\text{-C}^4$ is not equal to the expected value for the straight line: 180° . Due to the zigzag structure of the alkyl chain, this angle should be close to «tetrahedral», ie, to have value of about $109 - 110^\circ$. It is reasonable to expect that the repulsion of two volumetric tert-butyl groups (or more precisely, 18 hydrogen atoms of six methyl fragments, which are located in a relatively small space in the segment **ω -layer**) should increase value of this angle. However such increasing (as we expect), should not be very significant (maximum, within the limits of 10° , ie up to an angle value of not more than 120°).

In the **inner layer (α -layer)** are located both two carbon atoms C^2 and C^4 , which form the considered angle $\text{C}^2\text{-C}^3\text{-C}^4$ (along with two hydrogen atoms, **H-C^3**). They are come closer together in space, due to the relatively small the above angle $\text{C}^2\text{-C}^3\text{-C}^4$ between them ($\sim 110^\circ - 120^\circ$). Therefore, this **closeness in the space of six methyl groups, each of which grows from the atoms C^2 or C^4 , caused, in our view, *the increasing in the chemical shift* $\delta_{\text{CH}_3}^{\text{H}}$ of the 18 methyl protons of both tert-butyl groups, as the result of their **spatial repulsion****. Therefore, the differential parameter $\Delta\delta_{\text{CH}_3}^{\text{H}}$ ⁴⁴⁰⁰ increases to the value **+100 mlrd.** [In this case, however, not observed any change of the differential parameter $\Delta\delta_{\text{H}}^{\text{H}}$ of protons from the inner layer **H-C^3** (cf. $\Delta\delta_{\text{H}}^{\text{H}}$ ²²⁰⁰ = **-10 mlrd.** and $\Delta\delta_{\text{H}}^{\text{H}}$ ⁴⁴⁰⁰ = **-10 mlrd.**).

The **transition** from «quasi-linear» **L** alkane **4400** to «quasi-spherical» **I, QI**, alkane **4410**, which is considered above five-step path is the first step, means the replacement of a hydrogen atom from an inner layer H-C³ onto methyl group, i.e., the introduction onto «dicarbonicbranched» linear molecule **L** of alkane **4400** the **third** (albeit shortened) **carbonic branch** with forming of «threecarbonicbranched» alkane molecule **4410**. That is the transition from L (more precisely, from quasi-linear molecule of alkane) to **QI** alkane. It revealed that the introduction of such additional carbon branch **did not change** the value of the differential parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ ⁴⁴¹⁰, which also is equal to **+100 mlrd.**, ie, it had no effect on values of considered differential parameters. Further **transition** on the second stage, from **QI** alkane **4410** to the **Min I** alkane **4411**, followed by an introduction to the «threecarbonicbranched» alkane molecule **4410** yet the **fourth «carboncontaining branch»** (with forming of «tetracarbonicbranched» alkane molecule **Min I**), also almost did not change the value of the differential parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ ⁴⁴¹¹, which is equal to **+110 mlrd.**

Thus, it can be stated that replacement of two hydrogen atoms **H-C³** from an inner **α -layer** onto two methyl groups are practically **not accompanied** by changes in the studied parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ ⁴⁴ⁿ³ⁿ⁴ characterizing the 18 methyl protons of the two tert-butyl groups, located on the outer **ω -layer**. And only a further substitution of two **methyl** groups from the **third and fourth carbon branches** to the **ethyl** groups in the transition in the third stage from **Min I** alkane **4411** to **Max** alkane **4422** (where the parameter **H _{ω}** already is not **18**, but **24**), accompanied by a significant increase in the differential parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ ⁴⁴¹¹ from (**+100 mlrd.**) \rightarrow **4411 (+110)** \rightarrow **4422 to (+180)**.

Below we will try to give our explanation of these phenomena.

III. 5. 2. The relationship of ethylcontaining spherical alkane's structure with the values of differential spectral parameters $\Delta\delta^{\text{H}}_{\text{CH}_3}$ of ethyl fragments.

Now let us consider the most simple of all the compounds studied by us – the «true linear» alkane **2200** - n-pentane. Its molecule as the molecule of the aforementioned di-tert-butylmethane **4400** also has a **zigzag shape**. But the angle **C²-C³-C⁴**, we are interested in, as it is logical to assume, expect to be lesser than the same angle in **4400**. It can be expected that the repulsion of two small methyl groups (**C¹H₃** and **C⁵H₃**), which are located in the **outer ω -layer**, will be much less than comparable repulsion in the same **ω -layer** of two volumetric tert-butyl groups in di-tert-butylmethane **4400**. Therefore, in the «true linear» alkane **2200** such «lesser repulsion» much weaker «move apart» the angle **C²-C³-C⁴**, we are interested in, from «tetrahedral» value.

But the most important thing is this. In alkane **2200** each of the two carbon atoms **C²** and **C⁴** (these atoms are located in the inner **α -layer** along with **two hydrogen atoms**) is **bonded** with **only one methyl group** (either **C¹H₃** or **C⁵H₃**, six hydrogen atoms of which are located in the **ω -layer**). Unlike, in the above discussed alkane **4400** in **outer ω -layer** placed 18 hydrogen atoms of **six methyl groups**, which are come closer together in space (as shown above). Because of such «free opportunities» to choose the most comfortable position in space in the **outer ω -layer** for six hydrogen atoms in alkane **2200**, the **repulsion between two methyl groups** (**C¹H₃** and **C⁵H₃**) **should be minimized**. That is, just the **lack of spatial repulsion between the hydrogen atoms of the methyl groups in the ω -layer** **does not result**, in our view, to **an increase in the chemical shift $\delta^{\text{H}}_{\text{CH}_3}$ value** of the protons of two methyl groups (**C¹H₃** and **C⁵H₃**).

As stated above, the replacement of one of the two hydrogen atoms **H-C³** onto the alkyl group (methyl, first, and then ethyl *et al.*), ie, the transition **2200** \rightarrow **2210** (and other) transfer the alkyl compound **from the category of quasi-linear L alkanes to the category of quasi-spherical alkanes (QI)**.

Let us analyze hypothetically the most likely variant (in our view) of the possible influence of such a replacement (from **H** onto **CH₃**) on the studied parameter $\Delta\delta^{\text{H}}_{\text{CH}_3}$ of ethyl groups. By analogy to the above discussed for the alkane **2200** and **4400**, it is logical to expect that the more bulk than a hydrogen atom, the methyl group bonded to the **C³** (branch **b**), will **promote** an increase in **QI**

alkane **2210** the magnitude of angle $C^2-C^3-C^4$, which is interest to us, compared to **L** alkane **2200**. That is, as can be expected, this should help to increase the value of the parameter $\Delta\delta^H_{CH_3}$ of ethyl group, or, in other words, its transition into the «red zone».

The same effect (but in a still larger amount) it is logical to expect in the transition to the **Min I** alkane **2211**, which is formed from **2210** by replacing of the next (second) hydrogen atom $H-C^3$ onto the second methyl group. A similar but even greater on the value effect we assumed in the further introduction of each of the dicarbonic fragments **B** (Et, Prⁱ, Bu^t), especially of tert-butyl group as the third and fourth branches. As a result, it is logical to expect that there will be a gradual increase of the parameter $\Delta\delta^H_{CH_3}$ value of ethyl group, ie, «sure» *transition of it into the "red zone."*

In fact, there is quite the opposite picture.

The analysis of summarized in Table 13 parameters $\Delta\delta^H_{CH_3}$ values of ethyl, isopropyl and tert-butyl groups (as well as «ethyl» parameters $\Delta\delta^H_{CH_2}$) in the «spherical» alkanes, in which the total number of hydrogen atoms in the outer layer (parameter H_ω) does not exceed 15 shows that most of parameter $\Delta\delta^H_{CH_3}$ values (and much of parameter $\Delta\delta^H_{CH_2}$ values) in «spherical alkanes» are negative by sign. That is, most of the $\Delta\delta^H_{CH_3}$ (and $\Delta\delta^H_{CH_2}$) values are not in the red zone, but in the «green zone», what is more, the numerical values of some of them are very large. (Conversely, the numerical values of «red» parameters are very small, except of parameter $\Delta\delta^H_{CH_2}^{Et}$ ⁴²²¹).

And it is obvious the relations between the above amount and quality of branches, bonded to C^3 (**b** and **B**) and studied $\Delta\delta^H_{CH_3}$ parameters, as well as relations between the amount H_ω and $\Delta\delta^H_{CH_3}$.

Table 13

The dependence of parameter values $\Delta\delta^H_{CH_3}$ of hydrogen atoms in the ω -layer (as well as $\Delta\delta^H_{CH_2}$ in the β -layer) on the values **b**, **B** and H_ω (at $H_\omega \leq 15$).

Nvber of substance	Code of substance	3-d branch	4-th branch	H_ω	$\Delta\delta^H_{CH_3}$			X	$\Delta\delta^H_{CH_2}^{Et}$
					$\Delta\delta^H_{CH_3}^{Bu}$	$\Delta\delta^H_{CH_3}^{Pr}$	$\Delta\delta^H_{CH_3}^{Et}$		
1	2210	b	-	6	-	-	-20	X	-40
2	2211	b	b	6	-	-	-30	X	-70
3	2220	B	-	9	-	-	-40	X	+10
4	2221	B	b	9	-	-	-120	X	-80
5	3210	b	-	9	-	-50	-90	X	-40
	3211	b	b	9	-	н.д.	н.д.	X	н.д.
6	2222	B	B	12	-	-	-150	X	-100
7	3220	B	-	12	-	-50	-	X	-10
	3221	B	b	12	-	н.д.	н.д.	X	н.д.
	4210	b	-	12	н.д.	-	н.д.	X	н.д.
8	4211	b	b	12	-20	-	-50	X	+50
9	3310	b	-	12	-	-40	-	X	-
10	3311	b	b	12	-	-70	-	X	-
	3222	B	B	15	-	н.д.	н.д.	X	н.д.
11	4220	B	-	15	-30	-	+40	X	+20
12	4221	B	b	15	-20	-	-50	X	+100
13	3320	B	-	15	-	-20	+30	X	-20
	3321	B	b	15	-	н.д.	н.д.	X	н.д.
14	4310	b	-	15	-10	-50	-	X	-
15	4311	b	b	15	+20	+10	-	X	-

Absolutely different situation arise with a further increase of the parameter H_{ω} . If the total number of hydrogen atoms on the outer layer increases to values $H_{\omega} = 18$ and above, so, as seen from Table 14, almost all of the parameter $\Delta\delta_{CH_3}^H$ values (and all parameters $\Delta\delta_{CH_2}^H$) of «spherical» alkanes, conversely, get the positive values, ie., moving into the «red zone».

Table 14

The dependence of parameter values $\Delta\delta_{CH_3}^H$ of hydrogen atoms in the ω -layer (as well as $\Delta\delta_{CH_2}^H$ in the β -layer) on the values b , B and H_{ω} (at $H_{\omega} \geq 18$).

Nuvber of substance	Code of substance	3-d branch	4-th branch	H_{ω}	$\Delta\delta_{CH_3}^H$			X	$\Delta\delta_{CH_2}^H$ Et
					$\Delta\delta_{CH_3}^H$ Bu	$\Delta\delta_{CH_3}^H$ Pr	$\Delta\delta_{CH_3}^H$ Et		
1	4222	B	B	18	+30	-	+30	X	-
2	4320	B	-	18	+10	-10	+80	X	+50
3	4321	B	b	18	+50	+90	-10	X	+150
	4322	B	B	21	-	н.д.	-	X	н.д.
	4330	B	-	21		н.д.	-	X	-
4	4331	B	b	21	+110	+130	-	X	-
	4332	B	B	24		н.д.	н.д.	X	н.д.
	4333	B	B	27		н.д.	-	X	н.д.
5	4410	b	-	18	+100	-	-	X	-
6	4411	b	b	18	+110	-	-	X	-
7	4420	B	-	21	+100	-	+90	X	+40
	4421	B	b	21	н.д.	-	н.д.	X	н.д.
8	4422	B	B	24	+180	-	+140	X	+120
9	4430	B	-	24	+270	+270	-	X	-
10	4431	B	b	24	+200	+280	-	X	-
	4432	B	B	27	н.д.	н.д.	н.д.	X	н.д.
	4433	B	B	30	н.д.	н.д.	-	X	-
11	4440	B	-	27	н.д.	+350	-	X	-
	4441	B	b	27	н.д.	-	-	X	-
	4442	B	B	30	н.д.	-	н.д.	X	н.д.
	4443	B	B	33	н.д.	н.д.	-	X	-
	4444	B	B	36	н.д.	-	-	X	-

Given the above, let us comment now the course of considered above sequence of parameter $\Delta\delta_{CH_3}^H$ of tert-butyl group changes in transition: 4400 \rightarrow 4410 \rightarrow 4411 \rightarrow 4422.

We paid attention, that the stage: 4400 \rightarrow 4410 was not accompanied by an increase of the parameter $\Delta\delta_{CH_3}^H$, which, according to the above logic, to be expected. We put forward the following explanation. The expected increase of parameter $\Delta\delta_{CH_3}^H$ is compensated by a decrease of it due to the transition from the category of quasi-linear alkanes (L) «sphericity» to the category of quasi-spherical alkanes (QI) «sphericity». It can be assumed, that both options were roughly equal in size, and therefore «compensated» each other. Probably, practically the same situation also occurs in the transition: 4410 \rightarrow 4411. And only during the transition 4411 \rightarrow 4422 we observe effect of increasing of the spatial repulsion due to the replacement of two methyl groups on the two ethyl groups (as the third and fourth branches). This is because that the total number of hydrogen atoms on the outer layer increases to values $H_{\omega} = 24$, that **led to an increase** in the value of the parameter $\Delta\delta_{CH_3}^H$. This effect appears more significant in numerical terms than the effect of

increasing of the «sphericity» of the molecule with opposite sign, what resulting in the aggregated decrease in the value of the parameter $\Delta\delta_{\text{CH}_3}^{\text{H}}$.

III. 5. 3. The relationship of isopropylcontaining spherical alkane's structure with the values of differential spectral parameters $\Delta\delta_{\text{CH}}^{\text{H}}$ in transition: 4300 → 4310 → 4311 → 4320 → 4321.

We emphasize that $\Delta\delta_{\text{CH}}^{\text{H}}$ parameter refers to the methyne hydrogen of isopropyl group which is located in the intermediate β -layer. In the spherical isopropylcontaining alkanes its neighbors in the intermediate β -layer are hydrogen atoms of methyl groups (in short branches **b**), or any carbons anoms of long branches **B**. In quasi-linear (**L**) alkanes (3200, 3300, 4300) the neighbors in the intermediate β -layer – the carbon or the hydrogen atoms are absent.

Let us consider the relationship between the structure of spherical alkanes with parameters values $\Delta\delta_{\text{CH}}^{\text{H}}$ in the transition 4300 → 4310 → 4311 → 4320 → 4321. In the quasi-linear alkane 4300 due to lack of «carboncontaining neighbors in the intermediate β -layer» is intended the smallest parameter value $\Delta\delta_{\text{CH}}^{\text{H}}$ of all the members of the transition under consideration. Indeed, the value $\Delta\delta_{\text{CH}}^{\text{H} 4300} = +390$ mlrd. expectedly surpasses similar magnitude of simple (less branched) linear alkanes $\Delta\delta_{\text{CH}}^{\text{H} 3200} = +270$ mlrd and $\Delta\delta_{\text{CH}}^{\text{H} 3300} = +350$ mlrd. But it considerably less than similar parameters of quasi-spherical alkanes of the series under consideration, in which we have the third and / or the fourth carboncontaining branches (**b** or **B**): $\Delta\delta_{\text{CH}}^{\text{H} 4310} = +700$ mlrd., $\Delta\delta_{\text{CH}}^{\text{H} 4311} = +540$ mlrd., $\Delta\delta_{\text{CH}}^{\text{H} 4320} = +730$ mlrd., $\Delta\delta_{\text{CH}}^{\text{H} 4321} = +640$ mlrd. It is obvious that the replacement of the hydrogen atom in the intermediate β -layer on the alkyl group leads to a sharp increase of considered parameter $\Delta\delta_{\text{CH}}^{\text{H}}$. Note the observed twice decrease of parameter $\Delta\delta_{\text{CH}}^{\text{H}}$ at the transition from «threebranched» to «fourbranched» molecule structure: $\Delta\delta_{\text{CH}}^{\text{H} 4310} = +700$ → $\Delta\delta_{\text{CH}}^{\text{H} 4311} = +540$ mlrd. ($\Delta\Delta\delta_{\text{CH}}^{\text{H}} = (-160)$); and $\Delta\delta_{\text{CH}}^{\text{H} 4320} = +730$ → $\Delta\delta_{\text{CH}}^{\text{H} 4321} = +640$ mlrd. ($\Delta\Delta\delta_{\text{CH}}^{\text{H}} = (-90)$). It is logical to assume that this decrease is also due to the increasing degree of considered alkanes sphericity.

We can assume the following explanation with regard to large and very large positive values of all parameters $\Delta\delta_{\text{CH}}^{\text{H}}$ in isopropylcontaining spherical alkanes. The sole methyne hydrogen atom of isopropyl group is located in the intermediate β -layer. In this case «almost over it» in the external ω -layer necessarily located six hydrogen atoms of the two methyl groups of the isopropyl moiety. The presence of such «local screening», probably explains the observed large downfield shift of the signal under consideration. Here we see its fundamental difference of the parameters $\Delta\delta_{\text{CH}_2}^{\text{H}}$ of methylene hydrogen atoms of the ethyl group. In the ethyl fragment above two methylene hydrogen atoms «practically over them» in the external ω -layer necessarily located only three hydrogen atoms of sole methyl group. This probably is not enough to create a sufficiently effective «local screening», which would lead to a downfield shift of the methylene group protons signal.

Each of the remaining methyne hydrogen atoms H-C^3 [that are present only in molecules of quasi-spherical alkanes **Q** (**QI** and **QII**)] are located in the inner α -layer. As can be seen of each of 3 «concentric squares» drawing, which depicting molecules **QI** and **QII**, «practically over them» neither in intermediate β -layer nor in the outer ω -layer there are no any hydrogen atoms. Ie, the «local screening», which could determine the downfield shift of the signals of such protons (as in the case of methyne hydrogen atoms of isopropyl groups), is completely absent. Perhaps for this reason, a significant upfield shift of the considered signals of methyne hydrogen atoms H-C^3 , which located in the inner α -layer in molecules of quasi-spherical alkanes **Q**, occur be observed.

III. 5. 4. The hypothesis, we put forward to explain the above unexpected results.

To explain these unexpected results, we **put forward the assumption**, that the **«spherical» molecular structure of certain types of organic compounds (including the «spherical» alkanes) can specially affect** on the **values of proton chemical shifts of hydrogen atoms, that are inside this sphere**. Along with the «spherical» alkanes the similar effect we observed in a number of other classes of organic compounds: in the alcohols, carbonyl and carboxyl compounds, amines, as will be discussed later.

The essence of our assumptions is as follows. **Three** and especially **four carboncontaining branches** radiating from the **central carbon atom** (C^3) of the spherical alkane molecules **interact with one another**, similar to the **interaction of two or more heteroatoms in the case of «anomeric effect» of compounds with the heteroatoms, locating in geminal positions**. The existence of similar effect suggested by us earlier in disubstituted methanes of the general formula **X-CH₂-Y** and trisubstituted compounds **CHXYZ** [9].

The proposed hypothetical **interaction leads**, in our opinion, to upfield **shift of the signals of protons**, which **located inside the volume of «spherical ball» of the «spherical» molecule**.

IV. Conclusions

1. We propose the concept of the spherical (or «ball-shaped») compounds. In this communication we are considered NMR 1H spectra of 53 «spherical pentanes» - saturated hydrocarbons with a maximum length of the chain of five carbon atoms. Depending on the alkane sphericity these include substances from simplest n-pentane to most complicated tetra-(tert-butyl)methane.
2. We introduce the conception of the spherical alkane structure, which includes: a) a central carbon atom of the whole molecule (C^3), b) two, three or four carboncontaining branches attached to it. These include monocarbonic methyl (Me) and dicarbonic (longest chain) Et, Prⁱ, Bu^t- fragments. Besides of carboncontaining branches one or two branches may be the hydrogen atoms.
3. The central atom (C^3) is surrounded by three layers, called: a) inner - α -layer, b) intermediate - β -layer, and c) the outer - γ -layer, which is often referred to - ω -layer. The inner and intermediate layers may contain both carbon and hydrogen atoms, but the outer layer contain only hydrogen atoms. We consider several types of alkanes sphericity: «quasi-spherical», «minimally-spherical», and «maximally-spherical», as well as linear (n-pentane) and «quasi-linear».
4. We consider the values of proton chemical shifts in all 53 investigated spherical alkanes depending on the location of the studied hydrogen atoms in a certain layer.
5. It has been shown that the number of hydrogen atoms in the outer ω -layer (denoted by the symbol H_ω) and the uniformity of their distribution in the volume of this outer layer (which depends on the type of alkane sphericity) have a significant influence on the studied values of proton chemical shifts in spherical alkanes.
6. It has been shown that when parameter $H_\omega = 12$ (or 15) we observe the maximal upfield signals shift of all studied protons, except the methyne hydrogens of isopropyl group. Then, with the growth of H_ω parameter we observe an increase of the chemical shifts (downfield shift). It is shown that when the magnitude H_ω is equal to 12 (or 15) we observe for the methyl groups of ethyl fragments in the maximally-spherical compounds the highest upfield shift relative to the accepted standard (the $\delta^H_{CH_3}$ value of terminal methyl groups of linear long chain alkanes). The same also applies to methylene groups of ethyl fragments.

7. To explain the observed results, we propose the hypothesis, which is associated with the assumption of interaction to each other of three (or especially four) carbon-containing branches, radiating from the central carbon atom C^3 in spherical molecules. This interaction, in our opinion, is similar to the interaction (which we propose earlier) of two (in \underline{CH}_2XY) or three (in \underline{CHXYZ}) heteroatoms in the case of «anomeric effect» in compounds with gem-location of heteroatoms X, Y, Z . Namely this interaction, in our opinion, causes the observable upfield shift of the methylene or methyne proton's signals.

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