The dependence of disubstituted methanes X-CH$_2$-X and X-CH$_2$-Y methylene protons (C$\underline{H}_2$) and trisubstituted methanes CHX$_3$ or X$_2$CH-Y methyne protons (C$\underline{H}$) chemical shifts on the nature of substituents X and Y in the ^{1}H NMR spectra.

An anomeric effect action?

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Abstract. The chemical shifts values δ^{H}_{CH2} in the PMR spectra of 40 disubstituted methanes of general formula **X**-CH$_2$-**Y** and δ^{H}_{CH} of 19 trisubstituted methanes **X$_2$**CH$_2$-**Y** analyzed. The separate analysis of compounds with the **same substituents** [**X** = **Y**= **-Het(R)$_m$**, Part I] and with the **different substituents** (**X** ≠ **Y**, Part II) conducted. All substituents **X** and **Y** divided into two groups depending on the position in the periodic table of elements of the heteroatom **Het**: in the first group **Het** is an element of second period (**N,O,F**); in the second group **Het** - element of higher periods (**P,S,Cl,Br,I**). The rule of the electronegativity additive effect of both substituents **X** and **Y** on the parameters δ^{H}_{CH2} and δ^{H}_{CH} suggested. Found that this suggestion not performed when both substituents **X** and **Y** are the heteroatoms of the second period. In this case, instead of the expected downfield shift of δ^{H}_{CH2} and δ^{H}_{CH} occurs their upfield shift. To explain this phenomenon, we hypothesized the certain action of the well-known gem-anomeric effect, apparently occurring also for parameters of ^{1}H NMR spectra.

Key words: di- and trisubstituted methanes, base and differential chemical shift of methylene (methine) protons, substituents **X** and **Y**, two groups of substituents.

> *Despite being separated by a saturated carbon, two geminal substituents can interact strongly. This phenomenon has become known as the anomeric effect ... Both energetic and structural consequences are often dramatically large.*
> *P.von Rague Schleyer, E. D. Jemmis and .W. Spitznagel. J. Am. Chem. Soc., 1985, 107, 6393.*

> *It is of interest that whereas the oxygen-fluorine interaction is attractive, the oxygen-chlorine interaction is repulsive. A qualitatively similar situation is seen in the comparison of oxygen-oxygen (CH$_3$O group) with oxygen-sulfur (CH$_3$S group).*
> *E.Eliel, Angew. Chem. (eng.), 1972, 739.*

In accompanied communication [1] we have observed that the action of such substituents **X**, as (**X** = **-OR**) and (**X** = **-NR$_2$**) at the carbon atom **C^1** in 1,2-disubstituted propanes of the general formula (**X**)-C^{1}H$^1{}_2$-C^{2}H^2(**Y**)-C$^3\underline{H}^3{}_3$ results in the **upfield shift** of the methyl protons absorption in ^{1}H NMR spectra (only if the substituent **Y** also contains heteroatom of second period) compared to unsubstituted analogues: C^{1}H$^1{}_3$-C^{2}H^2(**Y**)-C$^3\underline{H}^3{}_3$ (**X** = **H**). So, the next question arises: Does the **same** two (**n** = 2) or three (**n** = 3) **substituents X** in the compounds with similar formula cause the same effect? As for the substances with similar formula in the literature sources we use in there is an insufficient number of spectral data, we decided to study this question using more simple examples. The simplest example is monocarbonic structures of the general formula $\mathbf{C^1\underline{H}_{4-n}X_n}$ (where **X** are an oxygen- or nitrogen-containing fragments, **n** = 2 or 3). So we investigate the question: whether the case, when these substituents **X** are **located at the same carbon atom** $\mathbf{C^1}$ (i.e. in the geminal position relative to each other) cause the same effect on the absorption of the protons $\mathbf{\underline{H}_{4-n}}$, associated with this carbon atom $\mathbf{C^1}$?

Thus, as stated above we consider the proton's chemical shift of di- and trisubstituted **methane** derivatives – the simplest examples of one-carbon containing alkanes. With the aim to introduce more systematic into our discussion we research also the monosubstituted derivatives (**n** = 1), which is denoted in general as $\mathbf{CH_3X}$ (**I**). Then formula of disubstituted methane derivatives in general will $\mathbf{CH_2XY}$ (**II**), wherein the second substituent is designated as **Y**, and trisubstituted derivatives of methane - **CHXYZ** (**III**).

In the analysis of the spectral parameters of the compounds **I - III**, we concluded the advisability of a separate analysis of compounds with the **same substituents** and with the **different substituents**. Therefore, in the first part of this study we examined compounds with the **same "heteroatom-containing" substituents** [$\mathbf{X = -Het(R)_m}$], which are linked to the carbon atom $\mathbf{C^1}$ with the bond **C-Het** (the symbol «**Het**» denotes a heteroatom). Compounds with **different substituents** (**X and Y** = $\mathbf{-Het(R)_m}$, but $\mathbf{X \neq Y}$) discussed in the second part of the study. We restrict ourselves to the compound wherein **Het** as elected the members of **V**, **VI** and **VII** groups of the second and third (and higher for halogen atoms) periods.

Part I.

Particularities of protons chemical shifts in di- (CH_2X_2) and tri- (CHX_3) substituted methanes containing identical heteroatom substituents ($X = -HetR_n$)

1. Introduction

The selection of substituents **X** is due among other factors the presence of "sufficiently reliable" spectral data for selected compounds. Thus, in the first instance we study the substances in which the heteroatom (**Het**) is an element of the second period (**V** group - nitrogen, **VI** -group - oxygen, **VII** group - fluorine). Then we consider the phosphorus-, sulphur-, chlorine-, bromine- and iodine-containing compounds, where heteroatom (**Het**) is an element of the third (or higher in the case when **X** = **Br** and **I**) period.

Each of the four haloid substituents [$\mathbf{X = -Het(R)_m}$] is a monovalent atom, so does not cause problems on its structure, since it does not contain fragments **R**. Structure of other substituents **X**, which containing the divalent heteroatoms of **VI** group (**O**, and **S**), and particularly trivalent atoms of **V** group (**N** and **P**) have raised questions concerning the structure of atoms (or groups of atoms) of fragment **-R**, which are bonded remaining valences of heteroatom **Het** in the substituent ($\mathbf{-Het(R)_n}$). Should this be the hydrogen atoms (for example, when **-X** = $\mathbf{-NH_2}$, $\mathbf{-PH_2}$, **-OH**, **-SH**, where **R = H**), or it must be derivatives of alkyl groups (**-X** = $\mathbf{-NAlk_2}$, $\mathbf{-PAlk_2}$, **-OAlk**, **-SAlk**, where **R** = **Alk**)? And what kind of alkyl group: methyl {e.g., $\mathbf{-NH\text{-}CH_3}$ or [$\mathbf{-N(CH_3)_2}$] , $\mathbf{-O\text{-}CH_3}$, $\mathbf{-S\text{-}CH_3}$}, ethyl or any other? Or, maybe the group **R** (especially in the case of elements of **V** group) are introduced the oxygen atoms, for example, **X** = **-NO**, $\mathbf{-NO_2}$, $\mathbf{-P(O)(OR^1)_2}$?

Therefore, considering the spectral data, we decided to consider all four substituents, which contained methyl fragments [**-O-Me, -S-Me,** $\mathbf{-N(Me)_2}$ and $\mathbf{-P(Me)_2}$], as well as some substituent **X** of **V** group elements, which contained oxygen atoms {nitro group (**-NO_2**), as nitrogencontaining derivative and dietoxyphosphonate group [**-P(O)(OEt)$_2$**] as phosphorocontaining derivative}. Moreover, thanks to a sufficiently large number of available at our disposal spectral data we decide to introduce three more oxygen containing substituents **-OR**, namely hydroxyl (**-OH**), ethoxy (**-O-CH_2-CH_3**) and acetoxy [**-O-C(O)-CH_3**] group. Thus, in the first part of our communication we consider **13** substituents **X**, which listed below.

Considered protons chemical shifts in the ^{1}H NMR spectra of compounds **Ix – IIIx** designated as $\boldsymbol{\delta^H_{Nx}}$ (eg, $\boldsymbol{\delta^H_{IIx}}$). In the subscript «**Nx**» the capital letter «**N**» numbered compounds (**I - III**): **CH_3X** (**N = I**), **CH_2X_2** (**N = II**) and **CHX_3** (**N = III**), and a small letter «**x**» designated substituents **X** indicated by the following letters: (-NMe_2) «**a**», (-NO_2) «**b**», (-O-H) «**c**», (-O-Me) «**d**», (-O-Et) «**D**», (-O-Ac) «**e**», (-F) «**f**», (-PMe_2) «**g**», [-P(O)(OEt)$_2$] «**G**», (-S-Me) «**h**», (-Cl) «**j**», (-Br) «**k**», (-I) «**L**». Sometimes we use alternative (conventional) chemical shifts symbols, for example, $\boldsymbol{\delta^H_{CH3X}}$.

II. Experimental

As the two main sources of information, as before, we use: a) the data of internet site [2], and b) atlas of NMR spectra of Aldrich firm, denoting its reference [3]. Furthermore, just for this study we recruit spectral data of the sources [4 - 7] of varying degrees of reliability, what detail below. Table 1 summarizes selected experimentally found values $\boldsymbol{\delta^H_{Nx}}$ of compounds **Ix** – **IIIx**, lead with the accuracy of 0.01 ppm. The square brackets indicate the source of information; if the numeral of chemical shift is given without parentheses, the data are taken from the [2].

Table 1

The values of the chemical shifts $\boldsymbol{\delta^H_{NX}}$ in the compounds Ix – IIIx, ppm

Substituent **X**	Value $\boldsymbol{\delta^H_{CH3X}}$, in monosubstituted methanes **I**.	Value $\boldsymbol{\delta^H_{CH2X2}}$, in disubstituted methanes **II**.	Value $\boldsymbol{\delta^H_{CHX3}}$, in trisubstituted methanes **III**.
-NMe_2 (a)	**2.22 [5]**	**2.71 [3]**	**3.05**
-NO_2 (b)	**4.32**	**6.10 [6]**	**7.52 [6]**
-O-H (c)	**3.49 [5]**	**4.90 [4]**	**4.98 [4]**
-O-CH_3 (d)	**3.27 [5]**	**4.57 [3]**	**4.97 [3]**
-O-CH_2-CH_3 (D)	**3.22 [4]**	**4.68**	**5.17**
-O-C(O)-CH_3 (e)	**3.66**	**5.73**	**-**
-F (f)	**4.27 [5]**	**5.45 [5]**	**6.41[5]**
-PMe_2 (g)	**0.89**	**1.40 [7]**	**0.58 [7]**
-P(O)(OEt)$_2$ (G)	**1.47 [3]**	**2.45 [3]**	**-**
-S-CH_3(h)	**2.12**	**3.62 [3]**	**4.67 [3]**
-Cl (j)	**3.05**	**5.33**	**7.27**
-Br (k)	**2.68**	**4.94**	**6.82**
-I (l)	**2.16**	**3.87**	**4.90**

The values of the parameters $\boldsymbol{\delta^H_{CH3X}}$, $\boldsymbol{\delta^H_{CH2X2}}$ and $\boldsymbol{\delta^H_{CHX3}}$ for substituents **X** different from various sources, and these differences may be greater than the selected by us the value of permissible error equal to 0.20 ppm (See below). Therefore, in Table 1 we give the most reliable (in our opinion) numerals. If such figures are absent in both most commonly used sources of us [2, 3], we have to use information selected from other sources. Preference is given to the data, which indicated that the spectra of ^{1}H NMR were obtained in $CDCl_3$. That source is the relatively recently published book of R. Abraham et al. (2008) [4]. In the absence of relevant information in this book, the next one on the reliability of the source, we believe the book of Pretcsh et al. (2000) [5], although it is not specified in it the solvent, in which the obtained spectra ^1H NMR are given. In the absence of information in these books, we used data from other sources [6 - 7], with preference given to newer publications.

As stated above, the error in $\boldsymbol{\delta^H_{NX}}$ values, that are taken from the least reliable (in our opinion) sources can (according to our estimates) exceed the value, which we take by arbitrary decision (± 0.20 ppm). In addition, some of the figures (for example, setting $\boldsymbol{\delta^H_{IIIc}}$ = **4.98** ppm and especially $\boldsymbol{\delta^H_{IIIg}}$ = **0.58** ppm), even taking into account the above, still be questionable. Furthermore, for two methine derivatives $\boldsymbol{\delta^H_{IIIe}}$ and $\boldsymbol{\delta^H_{IIIG}}$ we not found spectral data.

III. Results and Discussion

Formation of mono- (**CH_3X, Ix**), di- (**CH_2X_2, IIx**) and trisubstituted (**CHX_3, IIIx**) methanes logically considered as result of three consecutive stages of substitution of hydrogen atoms in a molecule of methane under the scheme (1):

$$\mathbf{CH_4 \xrightarrow{1} CH_3X\ (I) \xrightarrow{2} CH_2X_2\ (II) \xrightarrow{3} CHX_3\ (III)} \qquad (1)$$

Although the subject of our interest is the search for regularities of chemical shift $\boldsymbol{\delta^H}$ change of the remaining "methane" hydrogen atoms in molecules **IIx** and **IIIx** on the number and the structure of substituents **X** in them, it seems logical to say a few words about monosubstituted compounds. These substances **Ix** are formed by the replacement of the first of the four hydrogen atoms in methane with substituent **X** = **-$HetR_n$**. This process we call "**first transition**". It is reasonable to calculate the difference between the value of the chemical shift of methyl group protons in **Ix** (parameter $\boldsymbol{\delta^H_{CH3X}}$) and the value of the chemical shift of methane protons (parameter $\boldsymbol{\delta^H_{CH4}}$). We call this difference as «***experimental value for the first transition***» of substituents **X**. It is indicated by the symbol $\boldsymbol{\Delta\delta^{H,X}_{1,e}}$ in equation 2:

$$\boldsymbol{\Delta\delta^{H,X}_{1.e} = \delta^H_{CH3X} - \delta^H_{CH4} = \delta^H_{CH3X} - 0.22} \qquad (2)$$

Calculations of parameters $\boldsymbol{\Delta\delta^{H,X}_{1,e}}$ for the various substituents **X** were held in the middle of twentieth century, and since then the results have not changed substantially. Information on the value of the parameter $\boldsymbol{\delta^H_{CH4}}$ in methane is absent in both major sources of our information; other sources give slightly different numerals. In this paper, we adopted for uniformity the value $\boldsymbol{\delta^H_{CH4}}$ = 0.22 ppm, taken from the book [4].

Disubstituted "methylene" compounds **IIx** are formed from monosubstituted derivatives **Ix** when replacing one of the three remaining hydrogen atoms by the second substituent **X** in the second stage (**second transition**) of overall process **$CH_4 \rightarrow \rightarrow \rightarrow CHX_3$ (III)**. By analogy with the first step of this process (**$CH_4 \rightarrow CH_3X$**) the "experimental" value of the **second transition**, indicated by the symbol $\boldsymbol{\Delta\delta^{H,XX}_{2,e}}$, is calculated as the difference of parameter $\boldsymbol{\delta^H_{IIx}}$ and $\boldsymbol{\delta^H_{Ix}}$ (equation 3):

$$\boldsymbol{\Delta\delta^{H,XX}_{2,e} = \delta^H_{CH2X2} - \delta^H_{CH3X}} \qquad (3)$$

Similarly, for trisubstituted "methine" compounds **IIIx**, formed from methylene derivatives **IIx** by replacing one of the two remaining hydrogen atoms in $-CH_2-$ fragment by third substituent **X** in the third step, the "experimental" values of the **third transition** $\boldsymbol{\Delta\delta^{H,XXX}_{3,e}}$ are calculated by equation (4) as the difference between parameters $\boldsymbol{\delta^H_{IIIx}}$ and $\boldsymbol{\delta^H_{IIx}}$.

$$\Delta\delta^{H,XXX}_{3,e} = \delta^{H}_{CHX3} - \delta^{H}_{CH2X2} \qquad (4)$$

The values of the calculated "experimental parameters" of each of the three transitions listed in Table 2. In addition, after the parameters of second ($\Delta\delta^{H,XX}_{2,e}$) and of third ($\Delta\delta^{H,XXX}_{3,e}$) transitions we give the percentage ratio of their magnitudes to the magnitude of the first transition. For the second transition, this parameter, labeled as «$\%\Delta_{2,e}$», is equal: 100% x ($\Delta\delta^{H,XX}_{2,e}$ / $\Delta\delta^{H,X}_{1,e}$). And for the third transition the parameter of percentage ratio is: $\%\Delta_{3,e}$ = 100% x ($\Delta\delta^{H,XXX}_{3,e}$ / $\Delta\delta^{H,X}_{1,e}$). The values of percentage ratios are rounded to the nearest digit multiples.

Percentages ratios $\%\Delta_{2,e}$ and $\%\Delta_{3,e}$ which are listed in the Table 2, for clarity, are designated depending on their magnitude with the various color and font size. Let's consider firstly the parameters $\%\Delta_{2,e}$ and $\%\Delta_{3,e}$, ie, **in the range of 50% to 100%.** The ratio from 81% to 100% are indicated in blue and a maximum font size (14); from 61% to 80% - in heavenly color and the smaller font size (12); from 51% to 60% - green and the smallest font size (11). For parameter values $\%\Delta_{2,e}$ and $\%\Delta_{3,e}$, ie, **in the range of 0% to 50%**, the other symbols taken: the figures in range from 40% to 49% are marked with pink color and font size (12); ratio value 39% or less - red and maximum font size (14).

Special mention should be on the value of the parameter $\Delta\delta^{H,ggg}_{3}$ = - 0.82 ppm ($\%\Delta_{3,e}$ = -122%), that instead of the expected value above zero, proved negative number. This means that the introduction of a third substituent «**g** = -P(CH$_3$)$_2$» instead of a hydrogen atom in molecule of **IIg**: (CH$_3$)$_2$P-CH$_2$-P(CH$_3$)$_2$, leads <u>not to **downfield shift**</u> of signal δ^{H}_{CHg3}, as one might expect on the basis of all other positive values of $\Delta\delta^{H,XXX}_{3}$ parameters (including <u>minimal, but still positive</u> value of the parameter $\Delta\delta^{H,ccc}_{3}$ = +0.08 ppm), but to **highfield**. One possible explanation for this we consider the possible existence of spatial effects in the sterically crowded molecule of [(PMe$_2$)$_3$]CH (**IIIg**). That's why we marked parameter $\Delta\delta^{H,ggg}_{3}$ in table 2 with yellow color and font size (16).

Table 2

The values of the parameters $\Delta\delta^{H,X}_{1}$, $\Delta\delta^{H,XX}_{2}$, $\Delta\delta^{H,XXX}_{3}$, (ppm) $\%\Delta_{2,e}$ and $\%\Delta_{3,e}$ (%) in the compounds Ix – IIIx.

Substituent **X**	The values of the calculated "experimental parameters" of first transition, $\Delta\delta^{H,X}_{1,e}$	The values of the calculated "experimental parameters" of second transition, $\Delta\delta^{H,XX}_{2,e}$	The percentage ratio parameter $\%\Delta_{2,e}$, %	The values of the calculated "experimental parameters" of third transition, $\Delta\delta^{H,XXX}_{3,e}$	The percentage ratio parameter $\%\Delta_{3,e}$, %
-NMe$_2$ (a)	**2.00**	**0.49**	**25**	**0.34**	**17**
-NO$_2$ (b)	**4.10**	**1.78**	**43**	**1.42**	**35**
-O-H (c)	**3.27**	**1.41**	**46**	**0.08 ?**	**2**
-O-CH$_3$ (d)	**3.05**	**1.30**	**43**	**0.40**	**13**
-O-CH$_2$-CH$_3$ (D)	**3.00**	**1.46**	**49**	**0.49**	**16**
-O-C(O)-CH$_3$ (e)	**3.44**	**2.07**	**60**	**-**	**-**
-F (f)	**4.05**	**1.18**	**29**	**0.96**	**24**
-PMe$_2$ (g)	**+0.67**	**+0.51**	**76**	**-0.82**	**-122**
-P(O)(OEt)$_2$ (G)	**1.25**	**0.98**	**78**	**-**	**-**
-S-CH$_3$(h)	**1.90**	**1.50**	**79**	**1.05**	**55**
-Cl (j)	**2.83**	**2.28**	**81**	**1.94**	**69**
-Br (k)	**2.46**	**2.26**	**92**	**1.88**	**76**
-I (L)	**1.94**	**1.71**	**88**	**1.03**	**53**

In spite of the approximate values in the Table 2 we can make the following no doubt conclusions.

1) The values of **all parameters of subsequent transitions are less than the values of parameters of the previous transitions** (exception is the parameter $\mathbf{\Delta\delta^{H,ggg}_3}$, which mentioned above). This means, that the percentage ratios of the parameters of these transitions are proper fractions (ie, the values of $\%\mathbf{\Delta_{2,e}}$ and $\%\mathbf{\Delta_{3,e}}$ are less than 100%).

2) All of the six **percentage ratios of the second transitions** (i.e., the parameters $\%\mathbf{\Delta_{2,e}}$) values in Table 2 for the **substituents X**, containing heteroatoms **Het** of **elements of the second period (N, O, F)** fall within at a **value less than 50 % (25% - 49%).** This means that the ***parameters of the second transition*** ($\%\mathbf{\Delta_{2,e}}$) for these substituents **X** are **less than half** as the parameters of the first transition. The same, but still largely applies to the value of the ***percentage ratio of the third transition*** ($\%\mathbf{\Delta_{3,e}}$ = **2%** ÷ **35%**), ie, the parameters of the third transition more than three times less then parameters of the first transitions.

3) On the other hand, all five **percentage ratios of the second transitions** ($\%\mathbf{\Delta_{2,e}}$) **values** for the **substituents X**, containing **heteroatoms of elements of the third** (and higher) **periods (P, S, Cl, Br, I)** fall within at a **values much more than 50%** (**71%** - **92%**). That is, the values of the ***second transition parameters*** for these substituents **X** is only ***slightly less than the values of the first transition parameters***. The same applies to the **percentage ratios values** of the **third transitions** ($\%\mathbf{\Delta_{3,e}}$ = **53%** ÷ **76%**).

Thus, the **main difference** between the substituents **X**, containing **heteroatoms Het of elements of the second period (N, O, F)** and the substituents **X** with **heteroatoms Het of elements of higher periods (P, S, Cl, Br, I)** is fundamentally different **percentage ratios of the second transitions ($\%\mathbf{\Delta_{2,e}}$)**, as well as the values of the **percentage ratios of the third transitions ($\%\mathbf{\Delta_{3,e}}$)**. This conclusion is important for further discussion.

Now we will try to find a correlation between the chemical shift $\mathbf{\delta^H}$ in compounds **Ix - IIIx** and the **electronegativity of heteroatoms Het** in the substituents **X = HetR$_n$**, especially for di- (**IIx**) and tri- (**IIIx**) substituted methanes. For a starting look at this correlation for the simplest of test compounds - monosubstituted methanes **Ix**, for what consider the data in Table 1 again. All compounds **Ix** we grouped by two group: a) a compound with **Het** – the elements of the **fifth group - nitrogen and phosphorus** and **sixth group - oxygen and sulfur**, and b) compounds with **Het** – elements of the **seventh group - halogen atoms**.

Shortly after the start of using of the proton magnetic resonance method in organic chemistry the dependence of the chemical shift $\mathbf{\delta^H_{CH3X}}$ in monosubstituted methanes $C\underline{\mathbf{H}}_3$-X on various parameters of substituent **X** was the subject of in-depth study, and so far, now this problem sufficiently developed. The main factor affecting the $\mathbf{\delta^H_{CH3X}}$ value in **Ix**, is the **electronegativity** (χ) of heteroatom **Het** in the substituent (**HetR$_n$**). These relationships (in the form of graphs or tables) are present in all textbooks on the application of the NMR method in organic chemistry. Most books contained a linear relationship $\mathbf{\delta^H_{CH3X}} - \chi$ only for compounds of group «b», ie, methanehalides $C\underline{\mathbf{H}}_3$-Hal (**Ix**, **X** = Hal). In some sources the rest of the compound **Ix** of group «a», wherein **Het** in **X** is **N, O, S**, etc. are considered also. However, point on the graph of these substituents, for example, **–NR$_2$**, deviate significantly from the straight line, that was built for the $C\underline{\mathbf{H}}_3$-Hal – the compounds of second group «b». For compounds $C\underline{\mathbf{H}}_3$-X with substituents of group «a» sometimes built the second (adverse) line, which has other direct linear correlation of dependence $\mathbf{\delta^H_{CH3X}} - \chi$. Given this and other abovementioned uncertainties in the choice of optimal groups **-R** in substituents of the structure [**X = Y = -Het(R)$_m$**], the consideration of dependencies

$\delta^{H}_{CH3X} - \chi$ for substituents **X** containing a heteroatom **Het** with a valency greater than one (i.e., atoms **O, S, N** and **P**) is not justified.

In our opinion, we can be confident enough to talk about the existence of **linear** dependence between the electronegativity of **halogen** heteroatoms in the substituents **X** and the magnitude of the chemical shift δ^{H}_{CH3X}. For other heteroatoms of group «a» in the substituents [**X = -Het(R)**$_{m}$], **such a relationship is also take place, but it is more complex than straight (linear).** This finding is very important and will used by us in the future.

As can be seen from Tables 1 and 2, the chemical shift values δ^{H}_{CH3X} for monosubstituted methanes **Ix** and the values of first transition parameter $\Delta\delta^{H,X}_{1,e}$ (each having a value of about 1 - 4 ppm), differ from each other by a constant and a relatively small amount 0.22 ppm (δ^{H}_{CH4} = 0.22 ppm). Therefore, for compounds of group «b» it seems that the **parameters of the first transition** $\Delta\delta^{H,X}_{1,e}$ must **be substantially the same linear dependence on the value of the electronegativity (χ) of heteroatom Het** in substituents (X = Hal), as well as parameters δ^{H}_{CH3X}. For multivalent heteroatoms **Het** (of group «a») in substituents [**X = -Het(R)**$_{m}$] the consideration of dependencies of $\delta^{H}_{CH3X} - \chi$ types for monosubstituted methanes **Ix**, and the consideration of dependencies of $\Delta\delta^{H,X}_{1,e} - \chi$ types for the first transitions parameters **are impractical**. For this it is enough to compare an exemplary of two sets of parameters for substituents **X**, containing a nitrogen atom as a heteroatom **Het** with the different fragments **R** in formula **X = -N(R)**$_{m}$: a) $\delta^{H,X}_{1a}$ = 2.22 ppm and $\Delta\delta^{H,X}_{1a,e}$ = 2.00 ppm (for **X** = -NMe$_2$); b) with the values of $\delta^{H,X}_{1b}$ = 4.27 ppm and $\Delta\delta^{H,X}_{1b,e}$ = 4.05 ppm (for **X** = -NO$_2$).

When analyzing the series of compounds **CH_4 → CH_3X (I) → CH_2X_2 (II) → CHX_3 (III)** all without exception substituents **-X** [both with monovalent heteroatom (halogens) and with polyvalent heteroatom] becomes apparent that the **rule of additive effect of heteroatoms electronegativity in the abovementioned substituent** X on the **chemical shift** δ^{H} is **not performed**. And the more of these substituents **-X** are in the molecule of a substituted methane (**IIx** or **IIIx**), the greater the contrast of experimental value of chemical shift and of the calculated additive values. Therefore, it is possible to put forward the following proposition:

The same heteroatoms N, O, F in the substituents **X** [**X** = **-N(R)**$_{m}$] in the di- and trisubstituted methane derivatives, ie, CH_2X_2 (IIx) and CHX_3 (IIIx) **can interact with each other**. The **result** of this interaction is the **reduction of their summary electronegativity**. This effect **resembles the (or is) anomeric effect** in its Iliel's broadest interpretation, i.e., **for the compounds of general formula X-CH2-Y**.

As a **result** of this **effect** is **decrease** of methylene (in **IIx**) or methine (in **IIIx**) **proton signals downfield shift** compared with the expected value.

Perhaps it is for this reason that the methane derivatives with identical substituents **CH_2X_2** (**IIx**) and **CHX_3** (**IIIx**) are among the most uncomfortable (unsuccessful) objects to calculate the chemical shifts using the additive schemes with constant values of "universal" increments for each substituent X (Schulery's approach). In an alternative approach Prëtsh *et al* [5] tried to circumvent this difficulty by introducing a set of individual increments ($Z_{\alpha,1}$, $Z_{\alpha,2}$ и $Z_{\alpha,3}$) for each type of carbon atoms (**CH_3** , **$-CH_2-$** и **>CH-**), that is, in fact for **each** of the abovementioned **transition**. However, in this case, the desire to create a universal method of calculation for all the proton's types of aliphatic compounds also encountered in the "inconvenience" of methane derivatives with identical substituents.

For di- and trisubstituted methane derivatives (**IIx** and **IIIx**) with the identical substituents **X** [**X = -Het(R)**$_{m}$], which contain heteroatoms **Het** of third and higher periods (**S, Cl, Br, I**) periods, the same effect or occurs to a lesser degree, or absent completely. More details on this subject will covered in the second part of the article, which devoted to di- (**IV**) and trisubstituted (**V**) methane derivatives with different substituents **X** and **Y**.

Part II.

Particularities of protons chemical shifts in di- (CH_2XY) and tri- (CHXXY) substituted methanes containing different substituents (X, Y = $-HetR_n$).

I. Introduction

In the first part of this communication we have considered the of methylene and methine protons chemical shift's particularities in methane derivatives with identical substituents **X** (**X** = **-HetR**$_n$; **Het** - heteroatom): **CH_2X_2** and **CHX_3** respectively. Some regularities of proton chemical shift values, depending on the location of heteroatoms **Het** in periodic system of elements were found. The question arises: Will the above regularities still keep in the di- (**CH_2XY,** designated as **IV**) and trisubstituted (**CHXYZ,** designated as **V**) methanes with different heteroatomcontaining substituents (**X, Y, Z = -HetR**$_n$)?

Due to the lack of "sufficiently reliable" spectral data we have to limit ourselves to only one type of trisubstituted methane derivatives of general formula **CHXYZ**, which are containing only two types of substituents, ie, compounds of general formula **CHXXY**; so these structures are indicated below as **V**. As in the first part of communication the two main sources of information used are [2] and [3]. And yet, due to the lack of "sufficiently reliable" spectral data which contained in our chosen sources of information [2] and [3] we forced to bring also the spectral data from the original papers available in the world literature. Although these data may be not sufficiently reliable, but all the same we could not find more such data for all of the desired compounds. Thus, we are not satisfied founded on today the number of substances **IV** and **V**, which shown in Tables 4 and 5. Therefore, it can be said that in this report we present all of our data to date, but further the search for the spectral data of the compounds of general formula **CH_2XY** and **CHXXY** continues.

For the reasons given above, we restrict ourselves to the compound wherein only the members of **V, VI** and **VII** groups of the second and third (or higher for halogen atoms) periods elected as **Het**. Thus, in the second part of communication we consider for the compounds **IVxy** only **11** (of **13** considered in first part) substituents **X** and **Y**, they listed lower. Due to lack of experimental data, we decided to exclude from systematic review two substituents **X** and/or **Y** - phosphorus derivatives **$-PMe_2$** (**g**) and **$-P(O)(OEtAlk)_2$** (**G**). However, as we have found some spectral data of some phosphonate containing compounds with **$-P(O)(OBu)_2$** group, we decide included in the Table № 4 these substances with no special number. In the Table 4 they are numbered as previous compounds with a stroke (for instance №№ **6^I**, **6^{II}**). For the compounds **Vxxy** due to the lack of spectral data for these compounds it was used more fewer number of substituents **X** and/or **Y** (calculated parameters of 8 substituents, used – of 7 substituents).

The proton's chemical shifts in ^{1}H NMR spectra of compounds **IV** and **V**, are designated as δ^H_{IVxy} (e.g. δ^H_{IVag}) or δ^H_{Vxy}. In some cases, due to the lack of spectral data for compounds with methyl groups [**R** = Me in **X** = **-Het(R)**$_m$] the compounds with ethyl or butyl groups (**R** = Et or **R** =

n-Bu) are used, which are designated stroke over the corresponding letter. Here we give all the designations of 11 used substituents **X** and **Y**: (-NMe$_2$) «**a**», (-NO$_2$) «**b**», (-O-H) «**c**», (-O-Me) «**d**», (-O-Et) «**D**», (-O-Ac) «**e**», (-F) «**f**», (-S-Me) «**h**», (-Cl) «**j**», (-Br) «**k**», (-I) «**L**».

Ia. Our method of calculation

Given that each of the compounds **IV** and **V** contains two different types of substituents (**X** and **Y**), it can assumed that **each substituent makes its additive contribution to the chemical shift** under consideration (δ^{H}_{IVxy} or δ^{H}_{Vxy}). Therefore, it seems appropriate to introduce the concept of partial **"universal calculation" parameter** for each substituent, which is denoted as $\Delta\delta^{H,X}_{N}$ ($\Delta\delta^{H,Y}_{N}$). These parameters are different for compounds **IV** ($\Delta\delta^{H,X}_{IV}$) and **V** ($\Delta\delta^{H,X}_{V}$). It is logical to assume that these same parameters can also applied for the calculation of the compounds **II** and **III**, where **all substituents** (**X**) are **identical**. Then we can calculate the magnitude of the protons chemical shift in the compounds $\mathbf{C\underline{H}_{4-n}X_n}$ (**II**, **n** = 2 or **III, n** = 3) according to the logic, given in the exemplary of disubstituted methanes **II** or **IV**. For disubstituted compounds **II** with identical substituents **X** ($\mathbf{C\underline{H}_2XX}$) the value of chemical shift δ^{H}_{CH2X2}, is equal to, on the one hand, the value of the chemical shift of methane δ^{H}_{CH4} plus values of the first and second transitions; on the other hand, it is also the same value of the chemical shift of methane plus twice value of **"universal calculation" parameter** for the disubstituted compounds, ie., $\Delta\delta^{H,X}_{IV}$:

$$\delta^{H}_{CH2X2} = \delta^{H}_{CH4} + \Delta\delta^{H,X}_{1} + \Delta\delta^{H,XX}_{2} = \delta^{H}_{CH4} + 2 \times \Delta\delta^{H,X}_{IV} \quad (5)$$

Reducing similar terms δ^{H}_{CH4} in the left and in the right sides of the equation 5, we find that

$$\Delta\delta^{H,X}_{1} + \Delta\delta^{H,XX}_{2} = 2 \times \Delta\delta^{H,X}_{IV} \quad (6)$$

Hence let's calculate the magnitude of the **"universal calculation" parameter** for the disubstituted compounds ($\Delta\delta^{H,X}_{IV}$) as the **half the sum of the values of the first and second transitions**:

$$\Delta\delta^{H,X}_{IV} = ½ \times (\Delta\delta^{H,X}_{1} + \Delta\delta^{H,XX}_{2}) \quad (7)$$

Similarly, the value of **"universal calculation" parameter** for trisubstituted compounds ($\Delta\delta^{H,X}_{V}$), will be equal **to the third part of the sum of the values of the first, second and third transitions**:

$$\Delta\delta^{H,X}_{V} = 1/3 \times (\Delta\delta^{H,X}_{1} + \Delta\delta^{H,XX}_{2} + \Delta\delta^{H,XXX}_{3}) \quad (8)$$

The calculated values of universal calculation parameters $\Delta\delta^{H,X}_{IV}$, which are calculated with an accuracy of 0.01 ppm for compounds **IVxy**, are given in Table 3 for **12** of **13** substituents **X** (with the exception of substituents **PMe$_2$**), considered in first part of communication . Here are the values of the 10 parameters $\Delta\delta^{H,X}_{V}$, calculated for substances **Vxxy**.

Table 3

The values of **"universal calculation" parameter** $\Delta\delta^{H,X}_{IV}$ and $\Delta\delta^{H,X}_{V}$ in compounds **IVxy** and **Vxxy**, ppm

Substituent **X**	The values of **"universal calculation" parameters** $\Delta\delta^{H,X}_{IV}$ for compounds **IVxy**	The values of **"universal calculation" parameters** $\Delta\delta^{H,X}_{V}$ for compounds **Vxxy**
-NMe$_2$ (a)	**1.25**	**0.94**
-NO$_2$ (b)	**2.94**	**2.43**
-O-H (c)	**2.34**	**1.59**
-O-CH$_3$ (d)	**2.18**	**1.58**
-O-CH$_2$-CH$_3$ (D)	**2.23**	**1.65**
-O-C(O)-CH$_3$ (e)	**2.76**	**-**
-F (f)	**2.62**	**2.06**
-P(O)(OEt)$_2$ (G)	**1.12**	**-**
-S-CH$_3$(h)	**1.70**	**1.48**
-Cl (j)	**2.56**	**2.35**
-Br (k)	**2.36**	**2.20**
-I (l)	**1.83**	**1.56**

A. The methylene compounds IVxy

I. General

Now, using the values $\Delta\delta^{H,X}_{IV}$ we can calculate the expected values of methylene protons in the **IVxy**. We have decided to use our own calculation's scheme. It is interesting to compare the calculated values obtained by our calculation's scheme (denoted as $\delta^{H,XY}_{IVc}$), with the experimental data (denoted as $\delta^{H,XY}_{IVe}$), we could find in the literature used by us.

Our calculated values $\delta^{H,XY}_{IVc}$ obtained using the equation 9 are:

$$\delta^{H,XY}_{IVc} = \delta^{H}_{CH4} + \Delta\delta^{H,X}_{IV} + \Delta\delta^{H,Y}_{IV} = 0.22 + \Delta\delta^{H,X}_{IV} + \Delta\delta^{H,Y}_{IV} \quad (9)$$

The number of possible combinations of **11** substituents **X** and **Y** in compounds of general formula **IV CH$_2$XY** is **55.** For **all 55 these compounds** the **calculated values of chemical shift of methylene protons** (parameter $\delta^{H,XY}_{IVc}$), as well as their calculation, are shown in Table 4. It also provides **all experimental data**, designated as $\delta^{H,XY}_{IVe}$, which we can found in the literature with source reference. In the last column of Table № 4 we locate the difference between experimental and calculated values. This parameter can be either positive or negative. Its value, depending on the structure of the substituents **X** and **Y** discussed in the last section.

As said above in some cases we additionally used the substances with next substituents **X** and **Y:** (-S-Et) «$\mathbf{h}^{I}$» and [-P(O)(OBu)$_2$] «$\mathbf{G}^{I}$». For substituents $\mathbf{X} = \mathbf{G}^{I}$ the "universal calculation" parameter $\Delta\delta^{H,X}_{IV}$ is taken to be equal to the value of the "universal calculation" parameter $\Delta\delta^{H,X}_{IV}$ for the substituents **X = G**, ie, $\Delta\delta^{H,G1}_{IV} = \Delta\delta^{H,G}_{IV} = \mathbf{1.12}$ ppm. Similarly, the value of the parameter $\Delta\delta^{H,h1}_{IV}$ is taken to be equal of parameter $\Delta\delta^{H,h}_{IV} = \mathbf{1.70}$ ppm. There are **5** such compounds, designated as $\mathbf{IVxy}^{I}$, their data is given at the end of the table.

All these values $(\delta^{H,XY}_{IVc})$* are given in Table 4 turquoise. In the last column of Table 4 we present the difference between the experimental ($\delta^{H,XY}_{IVe}$, if found), and the calculated ($\delta^{H,XY}_{IVc}$), values for compounds **IVxy**, that designated as the **differential parameter** $\Delta\delta^{H,(e-c)}_{IVxy}$. This differential parameter we give a red font in black brackets if it is positive, and green if it is negative. Font size is selected depending on the magnitude of the difference: for $\Delta\delta^{H,(e-c)}_{IVxy} < 0.20$ ppm font is 10; 0.20 ÷ 0.49 ppm - 11; 0.50 ÷ 0.99 ppm - 12; 1.00 ÷ 1.99 ppm - 14; 2.00 ppm and more - 16.

Thus, the Table № 4 shows **60** (**55** + **5**) calculated for the compounds **IVxy** parameters as well as the experimental data for **27** (**22** + **5**) parameters of these compounds.

We also compute the calculated parameters $\delta^{H,XY}_{IVc}$ using other calculation schemes, as well as calculated parameters are taken from the Internet. Results comparing them with calculated parameters obtained by our scheme, as well as with the experimental data, we hope to present later.

II. Experimental

Table 4

Experimental $\delta^{H,XY}_{IVe}$) and calculated ($\delta^{H,XY}_{IVc}$) chemical shift values of methylene protons in the compounds of the general formula IV and their difference.

Number	Code of compound	Substituents **X** and **Y**	Experimental value of parameters $\delta^{H,XY}_{IVe}$; [reference]	Calculated value of parameters $\delta^{H,XY}_{IVc}$	The differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$
№ 1	**IVab**	**-N(CH$_3$)$_2$ (a), -NO$_2$ (b)**	**no data**	0.22 + 1.25 + 2.94 = **4.41**	**-**
№ 2	**IVac**	**-N(CH$_3$)$_2$ (a), -O-H (c)**	**no data**	0.22 + 1.25 + 2.34 = **3.81**	**-**
№ 3	**IVad**	**-N(CH$_3$)$_2$ (a), -O-Me (d)**	**3.88 [8]**	0.22 + 1.25 + 2.18 = **3.65**	**(+0.23)**
№ 4	**IVaD**	**-N(CH$_3$)$_2$ (a), -O-Et (D)**	**4.09 [9]**	0.22 + 1.25 + 2.23 = **3.70**	**(+0.39)**
№ 5	**IVae**	**-N(CH$_3$)$_2$ (a), -O-Ac (e)**	**4.85 [10]**	0.22 + 1.25 + 2.76 = **4.23**	**(+0.62)**
№ 6	**IVaf**	**-N(CH$_3$)$_2$ (a), -F (f)**	**5.12 [8]**	0.22 + 1.25 + 2.62 = **4.23**	**(+1.03)**
№ 7	**IVah**	**-N(CH$_3$)$_2$ (a), -S-Me (h)**	**no data**	0.22 + 1.25 + 1.70 = **3.17**	**-**
№ 8	**IVaj**	**-N(CH$_3$)$_2$ (a), -Cl (j)**	**8.32 [3]**	0.22 + 1.25 + 2.56 = **4.03**	**(+4.29)**
№ 9	**IVak**	**-N(CH$_3$)$_2$ (a), -Br (k)**	**no data**	0.22 + 1.25 + 2.36 = **3.83**	**-**
№ 10	**IVaL**	**-N(CH$_3$)$_2$ (a), -I (L)**	**8.19**	0.22 + 1.25 + 1.83 = **3.30**	**(+4.89)**
№ 11	**IVbc**	**-NO$_2$ (b), -O-H (c)**	**no data**	0.22 + 2.94 + 2.34 = **5.50**	**-**
№ 12	**IVbd**	**-NO$_2$ (b), -O-Me (d)**	**no data**	0.22 + 2.94 + 2.18 = **5.34**	**-**
№ 13	**IVbD**	**-NO$_2$ (b), -OEt (D)**	**no data**	0.22 + 2.94 + 2.23 = **5.39**	**-**
№ 14	**IVbe**	**-NO$_2$ (b), -O-Ac (e)**	**5.65 [11]**	0.22 + 2.94 + 2.76 = **5.92**	**(-0.27)**
№ 15	**IVbf**	**-NO$_2$ (b), -F (f)**	**no data**	0.22 + 2.94 + 2.62 = **5.78**	**-**
№ 16	**IVbh**	**-NO$_2$ (b), -S-Me (h)**	**no data**	0.22 + 2.94 + 1.70 = **4.86**	**-**
№ 17	**IVbj**	**-NO$_2$ (b), -Cl (j)**	**5.92 [12]**	0.22 + 2.94 + 2.56 = **5.72**	**(+0.20)**
№ 18	**IVbk**	**-NO$_2$ (b), -Br (k)**	**5.75 [3]**	0.22 + 2.94 + 2.36 = **5.52**	**(+0.23)**
№ 19	**IVbL**	**-NO$_2$ (b), -I (L)**	**no data**	0.22 + 2.94 + 1.83 = **4.99**	**-**
№ 20	**IVcd**	**-OH (c), -O-Me (d)**	**4.75 [13]**	0.22 + 2.34 + 2.18 = **4.74**	**(+0.01)**
№ 21	**IVcD**	**-OH (c), -O-Et (D)**	**no data**	0.22 + 2.34 + 2.33 = **4.79**	**-**
№ 22	**IVce**	**-OH (c), -O-Ac (e)**	**no data**	0.22 + 2.34 + 2.76 = **5.32**	**-**
№ 23	**IVcf**	**-OH (c), -F (f)**	**no data**	0.22 + 2.34 + 2.62 = **5.18**	**-**
№ 24	**IVch**	**-OH (c), -S-Me (h)**	**no data**	0.22 + 2.34 + 1.70 = **4.26**	**-**
№ 25	**IVcj**	**-OH (c), -Cl (j)**	**no data**	0.22 + 2.34 + 2.56 = **5.12**	**-**
№ 26	**IVck**	**-OH (c), -Br (k)**	**no data**	0.22 + 2.34 + 2.36 = **4.9**	**-**
№ 27	**IVcL**	**-OH (c), -I (L)**	**no data**	0.22 + 2.34 + 1.83 = **4.39**	**-**
№ 28	**IVdD**	**-O-Me (d), -O-Et (D)**	**4.44 [14]**	0.22 + 2.18 + 2.23 = **4.63**	**(-0.19)**
№ 29	**IVde**	**-O-Me (d), -O-Ac (e)**	**no data**	0.22 + 2.18 + 2.76 = **5.16**	**-**
№ 30	**IVdf**	**-O-Me (d), -F (f)**	**no data**	0.22 + 2.18 + 2.62 = **5.02**	**-**
№ 31	**IVdh**	**-O-Me (d), -S-Me (h)**	**no data**	0.22 + 2.18 + 1.70 = **4.10**	**-**
№ 32	**IVdj**	**-O-Me (d), -Cl (j)**	**5.46**	0.22 + 2.18 + 2.56 = **4.96**	**(+0.50)**

№ 33	IVdk	-O-Me (d), -Br (j)	5.67 [3]	0.22 + 2.18 + 2.36 = **4.76**	(+0.91)
№ 34	IVdL	-O-Me (d), -I (j)	5.80 [3]	0.22 + 2.18 + 1.83 = **4.23**	(+1.57)
№ 35	IVDe	-O-Et (D), -O-Ac (e)	no data	0.22 + 2.23 + 2.76 = **5.21**	-
№ 36	IVDf	-O-Et (D), -F (f)	no data	0.22 + 2.23 + 2.62 = **5.07**	-
№ 37	IVDh	-O-Et (D), -S-Me (h)	no data	0.22 + 2.23 + 1.70 = **4.15**	-
№ 38	IVDj	-O-Et (D), -Cl (j)	5.51	0.22 + 2.23 + 2.56 = **5.01**	(+0.50)
№ 39	IVDk	-O-Et (D), -Br (j)	no data	0.22 + 2.23 + 2.36 = **4.81**	-
№ 40	IVDL	-O-Et (D), -I (j)	no data	0.22 + 2.23 + 1.83 = **4.28**	-
№ 41	IVef	-O-Ac (e), -F (f)	5.93 [15]	0.22 + 2.76 + 2.62 = **5.60**	(+0.33)
№ 42	IVeh	-O-Ac (e), -S-Me (h)	5.13 [3]	0.22 + 2.76 + 1.70 = **4.68**	(+0.45)
№ 43	IVej	-O-Ac (e), -Cl (j)	no data	0.22 + 2.76 + 2.56 = **5.54**	-
№ 44	IVek	-O-Ac (e), -Br (k)	5.80 [3]	0.22 + 2.76 + 2.36 = **5.34**	(+0.46)
№ 45	IVeL	-O-Ac (e), -I (L)	no data	0.22 + 2.76 + 1.83 = **4.81**	-
№ 46	IVfh	-F (f), -S-Me (h)	5.63 [16]	0.22 + 2.62 + 1.70 = **4.54**	(+1.09)
№ 47	IVfj	-F (f), -Cl (j)	no data	0.22 + 2.62 + 2.56 = **5.40**	-
№ 48	IVfk	-F (f), -Br (k)	no data	0.22 + 2.62 + 2.36 = **5.20**	-
№ 49	IVfL	-F (f), -I (L)	no data	0.22 + 2.62 + 1.83 = **4.67**	-
№ 50	IVhj	-S-Me (h), -Cl (j)	4.72 [3]	0.22 + 1.70 + 2.56 = **4.48**	(+0.24)
№ 51	IVhk	-S-Me (h), -Br (k)	no data	0.22 + 1.70 + 2.36 = **4.28**	-
№ 52	IVhL	-S-Me (h), -I (L)	no data	0.22 + 1.70 + 1.83 = **3.75**	-
№ 53	IVjk	-Cl (j), -Br (k)	5.17 [3]	0.22 + 2.56 + 2.36 = **5.14**	(+0.03)
№ 54	IVjL	-Cl (j), -I (L)	4.97 [3]	0.22 + 2.56 + 1.83 = **4.61**	(+0.36)
№ 55	IVkL	-Br (k), -I (L)	no data	0.22 + 2.36 + 1.83 = **4.41**	-
№ 6^{I}	IVaG^{I}	-N(CH$_3$)$_2$ (a), -P(O)[O-Bu^n]$_2$ (G)	2.93 [17]	0.22 + 1.25 + 1.12 = **2.59**	(+0.34)
№ 23^{I}	IVcG^{I}	-OH (c), -P(O)[O- Bu^n]$_2$ (G^{I})	3.70 [17]	0.22 + 2.34 + 1.12 = **3.68**	(+0.02)
№ 30^{I}	IVdG^{I}	-O-Me (d), -P(O)[O-Bu^n]$_2$ (G^{I})	3.64 [17]	0.22 + 2.18 + 1.12 = **3.52**	(+0.12)
№ 31^{I}	IVdh^{I}	-O-Me (d), -S-Et (h^{I})	4.46 [14]	0.22 + 2.18 + 1.70 = **4.10**	(+0.36)
№ 37^{I}	IVDh^{I}	-O-Et (D), -S-Et (h^{I})	4.50 [14]	0.22 + 2.23 + 1.70 = **4.15**	(+0.35)

III. Results and Discussion

Analysis of the data in Tables 4

IIIa. General

Let us first consider the data in Table 4. Compare the 27 **experimentally found values** of the methylene protons chemical shifts in compounds **IV** ($\delta^{H,XY}_{IVe}$) with **our calculated parameters** ($\delta^{H,XY}_{IVc}$). Let us divide these 27 compounds **IVxy** ***into three group***, basing on the findings of the first part of article with respect to the difference of **X** and **Y** substituent [**X (Y) = -Het(R)$_m$**] by the criterion of their heteroatom **Het** belonging to second or higher period of Periodic Table.

The first group includes eight compounds in which both substituents **X** and **Y** comprise heteroatoms from a second period. These are the following compounds: **IVad (№ 3); IVaD (№ 4); IVae (№ 5); IVaf (№ 6); IVbe (№ 14); IVcd (№ 20); IVdD (№ 28); IVef (№ 41)**. The second group includes 16 compounds in which one of the substituents (**X** or **Y**) contains a heteroatom from the second period, and the second substituent – from the third (or higher for halogens) periods: **IVaG^{I} (№ 6^{I}); IVaj (№ 8); IVaL (№ 10); IVbj (№ 17); IVbk (№ 18); IVcG^{I} (№ 23^{I}); IVdG^{I} (№ 30^{I}); IVdh^{I} (№ 31); IVdj (№ 32); IVdk (№ 33); IVdL (№ 34); IVDh^{I} (№ 37^{I}); IVDj (№ 38);**

IVeh (№ 42); IVek (№ 44); IVfh (№ 46). The third group includes the remaining 3 compounds, both of **X** and **Y** substituents comprise heteroatoms **Het** from the third (or higher halogens) periods: **IVhj (№ 50); IVjk (№ 53); IVjL (№ 54)**.

IIIb. The structure of substituents X and Y

Let us consider in more detail the structure of substituents **X** and **Y** of the general formula [**X (Y) = -Het(R)$_m$**]. If heteroatom **-Het** is a two- or trivalent element, the structure of fragments **R** becomes important in it. Above in first part, as an example, we have led a dimethylamino (**a**) and nitro (**b**) groups to illustrate the inappropriate comparison of substituents **X** (**Y**) with multivalent heteroatoms (**N, O, P, S**), for which there is a problem of choice of fragments **-R** structure, compared with the substituents, where the heteroatom **-Het** is monovalent element (-**Het** = **-Hal**). Perhaps the best fragment **-R** structure must be hydrogen atom but in literature is very little experimental information about such substituents. Despite this, we still managed to introduce a hydroxyl group (substituent «**c**») into consideration, although for it for the above reasons, there is very few examples. It was logical to replace a hydrogen atom in the **-R** moiety to an alkyl group. Therefore, for the oxygen atom as the heteroatom (**Het = O**), we have introduced two substituents («**d**» and «**D**») with the most common methyl and ethyl groups as fragments **-R** in substituent of the general formula **X (Y) = -Het(R)$_m$**. Similarly, for nitrogen and phosphorus atoms (**Het = N, P**) we use the methyl groups as fragments **R** (the substituents «**a**» and «**g**»). However, for the substituent «**g**» we still have not managed to find any examples of compounds **IVgy** or **Vggy** (**Vgyy**).

We have also been deemed appropriate to consider completely opposite to hydrogen atoms fragments **R** in the substituent **X (Y) = -Het(R)$_m$** - an oxygen atoms. So there substituents «**b**» and «**G**» arised, in which in the general formula **X (Y) = -Het(R)$_m$** as fragments **R** used oxygen atom: (-**Het** = **N**, **R = O**) in substituent «**b**» and more complex combination of fragments **R** (-**Het** = **P**, **R^1** = **O**, **R^2** = **R^3** = **O-Alk**, where **Alk = Et**, in the substituent «**G**» or **Alk** = **Bu^n**, in the substituent «**G^I**»). For these substituents were found experimental data, that we introduce into the discussion. For the same reason, we deemed it appropriate to introduce the substituent «**e**» [-**Het** = **O**, **R = -C(O)-Me**], wherein in formula **X = -Het(R)$_m$** as a fragments **R** used a more complex acetyl structure. For sulfur atom as a heteroatom (-**Het** = **S**), due to lack of spectral data at our disposal we was found impractical to introduce a resembling additional substituents **X** (the structures, for example, such as **Het** = **S**, **R^1** = **R^2** = **O**, **R^3** = **O-Alk**, or similar structures) which can be designated as "**H**".

Based on the foregoing, we divide the first two substituent groups into two subgroups each. The first subgroup will both groups of compounds, which contain only substituents «**a**», «**c**», «**d**», «**D**» and «**h**». The second subgroup will include compounds, which contain substituents «**b**», «**e**» and «**G**». Thus, in the first subset of the first group are 5 compounds **IVad; IVaD; IVaf; IVcd; IVdD**, while in the second subset - a 3 compound **IVae; IVbe** and **IVef**. Similarly, in the first subset of the second group are 9 compounds **IVaj; IVaL; IVdh^I; IVdj; IVdk; IVdL; IVDh^I; IVDj** and **IVfh**. And in the second subset of the second group - a 7compounds **IVaG^I; IVbj; IVbk; IVcG^I; IVdG^I; IVeh** and **IVek**. These separations into groups and subsets is important to us when compared experimentally obtained and calculated values of the methylene protons chemical shift of the in compounds **IVxy**, what is said below.

IIIc. The principles of calculated and experimental data comparison

As stated above, we believe that the alkyl group as a fragment «**R**» in the substituents «**a**», «**c**», «**d**», «**D**» and «**h**» is much better substitute the "ideal" fragment «**R**» - hydrogen atom, than oxygen-containing fragments «**R**» in the substituents «**b**», «**e**» and «**G**». Therefore, it seems preferable to a comparison **just these substituents** with monovalent halide atoms (**F, Cl, Br, I**), ie, considered as substituents «**f**», «**j**», «**k**», «**L**». This means that **comparisons within each of the first subsets of two substituent groups** (such as, for example, the compounds **IVaf** and **IVdk**) seems to us a **more qualitative** (ie, the information received is more reliable) than the comparison of second subsets (ie, the compounds **IVae** and **IVeh**).

In the compounds **IVxy**, which contain the both substituents **X** and **Y** of the first group (ie, «**a**», «**c**», «**d**», «**D**» and «**f**»), we can **expect the behavior of two different heteroatoms - elements of the second period** (**[-Het** in the substituents **X** and **Y**) which is **similar to the behavior of two identical heteroatoms - elements of the second period** (**[-Het** in the substituents **X** and **X**) in compounds **II**, which we discussed in the first part of this article. Therefore, our calculated parameters ($\delta^{H,XY}_{IVc}$) calculated from the above formulas 9 should not, in our view, differ significantly from the experimental data ($\delta^{H,XY}_{IVe}$). Conversely, we can **expect a significant difference between the calculated ($\delta^{H,XY}_{IVc}$) and experimental ($\delta^{H,XY}_{IVe}$) data** for those compounds, wherein the heteroatom **Het** in the substituent **X** - (**heteroatom - element of the second period**) and **Het** in the substituent **Y** (**hetero - element of the third period**) belong to different groups (see the first part of article).

To test these suggestions we introduce the following criterion of differences of calculated ($\delta^{H,XY}_{IVc}$) and experimental ($\delta^{H,XY}_{IVe}$) parameters. If the difference between them that we describe as the differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$, **is equal or exceeding a value of 0.5 ppm in absolute terms** (ie, $|\ \Delta\delta^{H,(e-c)}_{IVxy}\ | \geq 0.5$ ppm), there is **reason to discuss this difference as significant**. If the difference is less than ± 0.5 ppm, it may be due to experimental errors, and the discussion we do not always consider it appropriate. Rather high value of the "critical difference" (0.5 ppm compared to the commonly used value of our 0.1 ppm) selected by us because of the use literature experimental data of different reliability, as well as the use of different solvents in the obtaining of the PMR spectra.

III.1. Comparison of parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of the first subset of compounds IVxy first group

Here we discuss the parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of 5 compounds, differential values of which we give in parentheses (the colour and font size numbers, as in the above tables, depending on its magnitude): **IVad** (**+0.23**); **IVaD** (**+0.39**); **IVaf** (**+1.03**); **IVcd** (**+0.01**); **IVdD** (**-0.19**). Note that in almost all cases, the parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ is a positive number. As expected, in four of the five cases fulfilled the expected ratio: $|\ \Delta\delta^{H,(e-c)}_{IVxy}\ | < 0.5$ ppm That is, in these cases, **found no significant differences** between our calculated and experimental parameters, which confirms the suggested assumption for the **first subset of the first group**.

It should be specially said about the only exception - the fifth case - fluorotrimethylamine **IVaf**, where the parameter $\Delta\delta^{H,(e-c)}_{IVaf}$ = **+1.03** ppm. The compound **IVaf** belongs to the group of **IVay** monohalotrimethylamines, in addition to which besides of **IVaf** belong the discussed below chlorotrimethylamine **IVaj**, bromotrimethylamine **IVak** and iodotrimethylamine **IVaL**. These compounds, which are studied Boehme et al. [6], discussed below.

III.2. Comparison of parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of the second subset of compounds IV first group

Let us discuss briefly the parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ of 3 compounds: **IVae** (**+0.62**); **IVbe** (**-0.27**); **IVef** (**+0.33**). Absolute value of parameter $\Delta\delta^{H,(e-c)}_{IVae}$ exceeds 0.5 ppm; the two remaining parameter is less than this value. Because of the aforementioned significant differences of fragment **–R** in structure of acetoxyl substituent ("**e**" = **-O-R**) compared with hydrogen atom (**-R** = **-H**), we can not predict the magnitude of the differential parameters $\Delta\delta^{H,(e-c)}_{IVey}$ for compounds of this subgroup. However, it should be noted that two of the three parameters does not exceed the limit value (0.5 ppm), and the third parameter is only slightly greater than this value.

III.3. Comparison of parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of the first subset of compounds IV second group

Let us discuss the parameter in parentheses $\Delta\delta^{H,(e-c)}_{IVxy}$ of 9 compounds: **IVaj** (**+4.29**); **IVaL** (**+4.89**); **IVdh^{I}** (**+0.36**); **IVdj** (**+0.50**); **IVdk** (**+0.91**); **IVdL** (**+1.57**); **IVDh^{I}** (**+0.35**); **IVDj** (**+0.50**) and **IVfh** (**+1.09**). Let us note that in all cases, the parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ is a positive numeral. As expected, in five of the nine cases, performed the expected ratio: $| \Delta\delta^{H,(e-c)}_{IVxy} | > 0.5$ ppm. Also in the two cases, the parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ exactly equal to the boundary value we choose (0.5 ppm). More in two cases, a ratio of $0.35 < | \Delta\delta^{H,(e-c)}_{IVxy} | < 0.5$ ppm is observed, ie, the parameters discussed only insignificantly less than the limit value (see also below). In this regard, we can recall that the limit value (0.50 ppm) was arbitrarily set by us, so it is not known how it corresponds to reality.

Therefore, it is logical to conclude that in most cases (or even in all 9 cases) we **found a significant difference** between our calculated and experimental parameters, which confirms the suggested assumption for the **first subset of the second group**.

Let us consider in more detail the group of monohalogenated trimethylamines of general formula $Me_2N\text{-}CH_2\text{-}Hal$, which includes fluoroderivative **IVaf**, discussed above, as well as chloro- (**IVaj**), bromo- (**IVak**) and iodo- (**IVaL**) trimethylamines. It suggested that the last three compounds being solid crystalline materials exist in the form of so-called «inner salt»: $[Me_2N^+=CH_2]\ Hal^-$. That is why the absorption of the vinyl protons in $N^+=CH_2$ fragment strongly shifted to low field (up to values of $\delta^H = 8 \div 9$ ppm), resulting in dramatically increasing (to a value of +4.0 ppm and above) the discussed differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$. The same structure is expected for similar "internal salts" of the general formula: $[Me_2N^+=CH_2]\ A^-$, derivatives of strong acid (HA), where the anion $A^- = CF_3COO^-$, CCl_3COO^-, etc. On the other hand, when acid HA is weak or moderate in strength acid, the structure of the compounds under consideration is not salt-like, as they are relatively low-boiling liquids. That, such compounds are the above-considered compounds $Me_2N\text{-}CH_2\text{-}F$ (**IVaf**) and $Me_2N\text{-}CH_2\text{-}O\text{-}Ac$ (**IVae**). Interestingly, as a boundary between the salt-like and "homolytic" structures is the structure of sulphite $[Me_2N^+=CH_2]\ HSO_3^-$ [18]. Shown PMR spectra of it is obtained in trifluoroacetic acid and involves the simultaneous existence of both structures ($\delta^H_{CH2} = 4.57$ ppm and $\delta^H_{CH2} = 8.0$ ppm). The existence of compounds with the simultaneous presence of these two structures suggests the possibility of the transition from one structure to another. The question arises: Whether there is in the "homolytic" structure of monofluoro trimethylamine $Me_2N\text{-}CH_2\text{-}F$ (**IVaf**) a certain amount of salt-like mesomeric structure? If so, this fact can explain a slight increase in the magnitude of parameter $\Delta\delta^{H,(e-c)}_{IVaf}$ up to the value

+1.03 ppm. At the same time for dimethylamino methylacetate $Me_2N\text{-}CH_2\text{-}O\text{-}Ac$ (**IVae**), where perhaps percentage of saltlike mesomeric structure (if it exist) is less, we can expect a smaller value of the differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ under discussion. Indeed, the calculated value of the parameter $\Delta\delta^{H,(e-c)}_{IVae}$ = +0.62 ppm less than the debated value, $\Delta\delta^{H,(e-c)}_{IVaf}$ = +1.03 ppm.

III.4. Comparison of parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of the second subset of compounds IVxy second group

Let us discuss briefly the values of differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ of 7 compounds of the second subset of second group compounds **IV**: **IVaG^{I}** (**+0.34**); **IVbj** (**+0.20**); **IVbk** (**+0.23**); **IVcG^{I}** (**+0.02**); **IVdG^{I}** (**+0.12**); **IVeh** (**+0.45**); **IVek** (**+0.46**). Note, that the **magnitudes** of all these 7 parameters are positive numerals, which are **less than the limiting value of 0.50 ppm.**

III.5. Comparison of parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of the compounds IVxy third group

Now we discussed the values of differential parameters $\Delta\delta^{H,(e-c)}_{IVxy}$ of last 3 compounds **IVxy** third group: **IVhj** (**+0.24**); **IVjk** (**+0.03**) и **IVjL** (**+0.36**). Note that all parameter $\Delta\delta^{H,(e-c)}_{IVxy}$ are positive numerals, and thus fulfilled the expected ratio: $|\ \Delta\delta^{H,(e-c)}_{IVxy}\ | < 0.5$ ppm. That is, in these cases, **found no significant differences between our calculated and experimental parameters**, which **correspond to the expectations for the compounds of Group 3.**

B. The methine compounds Vxxy

II. Experimental

All that said about the structure of the table 4 and the designation of all the parameters ($\delta^{H,XXY}_{Vc}$, $\Delta\delta^{H,(e-c)}_{Vxxy}$ and others) is true for Table 5. Here given **<u>all 8 experimental data</u>**, designated as $\delta^{H,XXY}_{Ve}$, which we can found in the literature from the large number of possible variants. In the last column of Table № 5 we locate discussed parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ - the difference between experimental and calculated values.

Table 5

Experimental $\delta^{H,XXY}_{Ve}$) and calculated ($\delta^{H,XXY}_{Vc}$) chemical shift values of methine protons in the compounds of the general formula V.

N	Code of compound	Substituents **X** and **Y**	Experimental value of parameters $\delta^{H,XY}_{IVe}$; [reference]	Calculated value of parameters $\delta^{H,XY}_{IVe}$	The differential parameter $\Delta\delta^{H,(e-c)}_{IVxy}$
№ 1	**Vdda**	**-O-Me (d), -O-Me (d), -N(CH$_3$)$_2$ (a)**	**4.36 [3]**	**0.22 + 1.58 + 1.58 + 0.94 = <u>4.32</u>**	**(+0.04)**
№ 2	**VDDa**	**-O-Et (D), -O-Et (D), -N(CH$_3$)$_2$ (a)**	**4.52**	**0.22 + 1.65 + 1.65 + 0.94 = <u>4.46</u>**	**(+0.04)**
№ 3	**Vffd**	**-F (f), -F (f), -O-Me (d)**	**6.14 [19]**	**0.22 + 2.06 + 2.06 + 1.58 = <u>5.92</u>**	**(+0.22)**
№ 4	**Vjjb**	**-Cl (j), -Cl (j), -NO$_2$ (b)**	**7.40 [12]**	**0.22 + 2.35 + 2.35 + 2.43 = <u>7.35</u>**	**(+0.05)**
№ 5	**Vjjd**	**-Cl (j), -Cl (j), -O-Me (d)**	**7.34 [3]**	**0.22 + 2.35 + 2.35 + 1.58 = <u>6.50</u>**	**(+0.84)**
№ 6	**Vjjf**	**-Cl (j), -Cl (j), -F (f)**	**7.41 [20]**	**0.22 + 2.35 + 2.35 + 2.06 = <u>6.98</u>**	**(+0.43)**
№ 7	**Vjjk**	**-Cl (j), -Cl (j), -Br (k),**	**7.19 [3]**	**0.22 + 2.35 + 2.35 + 2.20 = <u>7.12</u>**	**(+0.07)**
№ 8	**Vkkj**	**-Br (k), -Br (k), -Cl (j)**	**7.06**	**0.22 + 2.20 + 2.20 + 2.35 = <u>6.97</u>**	**(+0.09)**

III. Results and Discussion

Analysis of the data in Table 5

By analogy with methylene compounds **IVxy** let us divide all 8 substances **Vxxy** into three groups. Additionally all compound of the second group is further divided into two subsets.

III.1. Comparison of parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ of compounds Vxxy first group

The first group consists of three compounds: **Vdda** (**+0.04**)**; VDDa** (**+0.06**) and **Vffd** (**+0.22**). All three compounds are included in a single first subset. Note that in all cases the differential parameter $\Delta\delta^{H,(e-c)}_{Vxy}$ is a positive number, and, as expected, the following relation holds: $|\ \Delta\delta^{H,(e-c)}_{Vxxy}\ | < 0.5$ ppm. **Absence of significant differences** between our calculated and experimental parameters **confirms the hypothesis** suggested for the compounds of the **first subset of the first group**.

III.2. Comparison of parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ of the first subset of compounds Vxxy second group

Here we discussed the values of differential parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ of 2 compounds of first subset of the second group: **Vjjd** (**+0.84**) and **Vjjf** (**+0.43**). Note that in both cases the differential parameter $\Delta\delta^{H,(e-c)}_{Vxxy}$ is a positive number. As expected, in **one case**, the **following relation holds**: $|\ \Delta\delta^{H,(e-c)}_{Vxy}\ | > 0.5$ ppm, while the second case the discussed parameter only insignificantly less than the limit value (0.43 vs. 0.50). Again, it may be recalled, on an **arbitrary selected limit value** (0.50 ppm), perhaps it would be better to set its value in the range 0.35 ÷ 0.40 ppm. In this case, the second parameter $\Delta\delta^{H,(e-c)}_{Vjjf}$ would be consistent with the expected values. This limit value (0.35 ÷ 0.40 ppm) would fit well also two dropped out of a number of parameters discussed above for the compounds of the 1-st subset of 2-nd group methylene derivatives **IVxy** ($\Delta\delta^{H,(e-c)}_{IVdh'} = 0.36$ ppm and $\Delta\delta^{H,(e-c)}_{IVDh'} = 0.35$ ppm).

Therefore, we can conclude that for compounds of the **1-st subset of the second group it is found a significant difference** between our calculated and experimental parameters, that **meet the assumption** put forward by us.

III.3. Comparison of parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ of the second subset of compounds Vxxy second group

For a single compound **Vjjb** of the second subset of compounds **Vxxy** second group the parameter $\Delta\delta^{H,(e-c)}_{Vjjb} = +0.05$ ppm is a positive number. Moreover this magnitude is much less of the boundary (limit) values, which we have adopted equal to 0.50 ppm (or 0.35 ÷ 0.40 ppm).

III.4. Comparison of the parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$ of the compounds Vxxy third group

Here we discussed the values of differential parameters $\Delta\delta^{H,(e-c)}_{Vxy}$ of 2 compounds of third group: **Vjjk** (**+0.07**) and **Vkkj** (**+0.09**). Both parameters are positive and has a very small amount, ie, the **expected ratio is executed**: $|\ \Delta\delta^{H,(e-c)}_{IVxy}\ | < 0.5$ ppm. That is, in these cases, **found no significant differences** between our calculated and experimental parameters, **in line with our expectations** for the **compounds of Group 3**.

* * *

Therefore, generalizing above-considered data for both types of we considered substance - **IVxy** and **Vxxy** - we can make the **main conclusion**: the differential parameters $\Delta\delta^{H,(e-c)}_{IVxy}$, calculated for 27 methylene compounds **IVxy**, as well as differential parameters $\Delta\delta^{H,(e-c)}_{Vxxy}$, calculated for 8 methine compounds **Vxxy**, in the main **correspond** to **our expected values**, we have calculated on the basis of **assumptions** about the **different (in magnitude) interaction** of heteroatoms (X and Y) of the ***second*** and ***third*** (and higher) period elements, when they are in the geminal position in fragment **X-CH-Y (X_2C-Y).**

So, when analyzing experimental and calculated spectral data for all 35 compounds **IVxy** and **Vxxy** becomes apparent that the **rule of additive effect of heteroatoms electronegativity** of located in the **geminal position** relative to each other the **substituents X** and **Y** on the **chemical shift of methylene (methane) protons** is **not performed in all cases**. Therefore, it is possible to put forward the following proposition:

The heteroatoms of second period - N, O - in the **substituents X** and **Y** located **in geminal position** in the disubstituted (**X-CH-Y**) and trisubstituted (**X_2C-Y**) methanes **can powerfully interact with each other**. The **result** of this interaction is the **reduction of their summary electronegativity**, which causes upfield shift of discussed parameter δ^{H}_{CHn}. This effect **resembles (or is) well-known gem-anomeric effect** in its broadest interpretation.

IV. General conclusions

Part I

1. We have analyzed the protons chemical shifts values δ^{H}_{CHn} in the PMR spectra of 13 series of polysubstituted methanes (**I - III**) of general formula **$CH_{4-n}X_n$** [where **X** are heteroatom-containing substituent (**X = -HetR$_n$**), **n** = 1, 2 or 3]. All substituents **X** divided into two groups depending on the nature of the heteroatom **Het**. In the first group - this is the heteroatom of the second period – **nitrogen, oxygen or fluorine**; in a second group – it is an heteroatom of third (or higher) periods: **phosphorus, sulfur, chlorine, bromine, iodine**. Formation of mono-, di- and trisubstituted methanes considered as result of three consecutive stages (named «transitions») **CH_4** → **CH_3X (I)** → **CH_2X_2 (II)** → **CHX_3 (III)**. The difference between the values of the chemical shift of methyl protons in **Ix** (δ^{H}_{CH3X}) and of methane (δ^{H}_{CH4}) called as value for the first transition of substituents **X** and indicated as $\Delta\delta^{H,X}_{1}$. Similarly calculated and tabulated parameters of the second ($\Delta\delta^{H,X}_{2}$) and third ($\Delta\delta^{H,X}_{3}$) transitions. A comparison of $\Delta\delta^{H,X}_{2}$ or $\Delta\delta^{H,X}_{3}$ with $\Delta\delta^{H,X}_{1}$ expressed in percent and is designated as $\%\Delta_{2,e}$ and $\%\Delta_{3,e}$ relatively.

2. We suggest the rule of the electronegativity additive effect for located in the geminal position substituents **X** on the chemical shift δ^{H}_{CHn} in di- and trisubstituted methanes, which implies the value of parameter $\%\Delta_2$ and $\%\Delta_3$ equal to 100%. However, the parameter $\%\Delta_{2,e}$ of the first group of substituents **X** (**Het = N,O,F**) do not exceed **50%,** and for a second group of substituents **X** (**Het = P,S,Cl,Br,I**) the values of $\%\Delta_{2,e}$ ranged from 70 to > 90%. More smaller quantities found for parameter $\%\Delta_3$: **2 – 35%** for first group; 50 -75% for second group. Thus, the **main difference** between the first and second groups of substituents **X** is fundamentally different percentage ratios of the second and third transitions.

3. We suggest that the same heteroatoms **N, O, F** in the first group of substituents **X** can **interact with each other**. The result of this is the **reduction of their summary electronegativity**, which causes **upfield shift** of discussed parameter δ^{H}_{CHn}. This effect resembles the **anomeric effect** in it broadest interpretation. As a **result** is **decrease** of methylene (in **IIx**) or methine (in **IIIx**) protons **signals downfield shift** (and accordingly, the decrease of parameters $\%\Delta_2$ and $\%\Delta_3$).

4. For compounds **IIx** and **IIIx** with the substituents **X** of second group (**Het** = **P**, **S, Cl, Br, I**) the same effect or occurs to a lesser degree, or absent completely.

Part II

1. We have analyzed the protons chemical shifts values δ^{H}_{CH2} in the PMR spectra of 27 substances of 11 series of disubstituted methanes (**IV**) of general formula **CH_2XY** [where **X** and **Y** are heteroatom-containing substituent (**X = Y = -HetR_n**, **X ≠Y**), described in Part I] and δ^{H}_{CH} of 8 compounds of trisubstituted methanes (**V**) of general formula **CHXXY**. We propose the method of chemical shifts values δ^{H}_{CH2} and δ^{H}_{CH} calculation, using the "universal calculation" parameter for each substituent, denoted as $\Delta\delta^{H,X}_{N}$ ($\Delta\delta^{H,Y}_{N}$). Parameters $\Delta\delta^{H,X}_{IV}$ and $\Delta\delta^{H,Y}_{IV}$ for disubstituted methanes **CH_2XY** (**IV**) calculated as half of the sum of first and second transition parameters $\Delta\delta^{H,X}_{1}$ and $\Delta\delta^{H,X}_{2}$, calculated above for disubstituted methanes **CH_2XX** (**II**) with identical substituents **X**. Similarly, as the third part of the sum of first, second and third transition parameters $\Delta\delta^{H,X}_{1}$, $\Delta\delta^{H,X}_{2}$ and $\Delta\delta^{H,X}_{3}$, calculated the "universal calculation" parameters $\Delta\delta^{H,X}_{V}$ ($\Delta\delta^{H,Y}_{V}$) for trisubstituted methanes **CHXXY** (**V**). In Tables 4 and 5 compared the calculated and experimental δ^{H}_{CH2} values.

2. As in part I, all substituents **X** and **Y** divided into two groups: (**Het = N,O,F**) in first and (**Het** = P, **S, Cl, Br, I**) in second group and suggested the rule of the electronegativity additive effect for located in the geminal position substituents **X** and **Y**. Compared three types of compounds **IVxy** and **Vxxy**. In the first type both substituents represent first group, in the third type- the second group; in the second type the substituents represent both different groups.

3. In the compounds **IVxy** of the first type (as in part I) we can expect the identical behavior of two different heteroatoms **-** elements of the second period. This will lead to the fact that our calculated parameters ($\delta^{H,XY}_{IVc}$) should not differ significantly from the experimental data ($\delta^{H,XY}_{IVe}$). A similar conclusion can assumed for the compounds of the third type. Conversely, we can expect a significant difference between the calculated ($\delta^{H,XY}_{IVc}$) and experimental ($\delta^{H,XY}_{IVe}$) data for compounds of second type due to the lack of alleged interaction between the substituents of first and second groups.

4. The majority of data in the Tables 4 and 5 basically confirm our assumptions. Therefore, the data for compounds **CH_2XY** (**IV**) and **CHXXY** (**V**) with different substituents **X** and **Y** confirm our assumptions about the existence of the **anomeric effect** for **parameters of ^{1}H NMR spectra** in it broadest interpretation.

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