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TOPOLOGICAL SCHEME FOR EMPIRICAL ESTIMATION OF ¹³C NMR CHEMICAL SHIFTS IN POLYBROMOALKANES

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Homolytic reactions of organic bromine compounds yield mixtures of polybromoalkanes that are isomeric or similar in structure; ¹³C NMR is an effective method for the identification of these compounds. Here a problem arises in distinguishing chemical shifts (CSs) that are quite characteristic for the various compounds but are very similar in magnitude [1].

In calculating the CS of carbon atoms in polysubstituted alkanes, the use of individual increments of heteroatoms as determined from ¹³C NMR spectra of monosubstituted compounds [2] is practically impossible unless the influence of substituent interaction on the CS can be taken into account. We had previously proposed a technique for reducing the error in empirical estimates of δ ¹³C in polyhaloalkanes (Cl and Br) [3] by introducing structural increments and also corrections for two-particle and three-particle interaction of halogen atoms. The set of corrections that we obtained gives a satisfactory description of the ¹³C NMR spectra of this class of compounds; however, the special character of these corrections impels us to seek a universal, accessible algorithmization of the method for empirical description of the magnitudes of δ ¹³C — one that will take into account the actual physical interactions between atoms in the molecule and will permit comparison of the influence of various functional groups.

In our previous studies, we found that the influence on δ^{-13} C from a substituent located at a distance of more than three bonds from the C atom under consideration is comparable in magnitude to the error in the empirical calculational schemes themselves, and this influence can be neglected. We also found that, within the framework of this error, the two-particle approximation proves to be adequate in analyzing the influence of collective properties of substituents on the CS of the carbon. This is important since any attempt to account for all three-particle interactions results in a catastrophic expansion of the increment scheme. In contrast, the number of two-particle combinations is limited, and such combinations are frequently encountered; therefore, their contributions are statistically more reliable — an important factor determining the predictive value of empirical schemes.

The present work has been aimed at finding an equation linking the topological image of a molecule with experimental values of $\delta^{13}C$ in polybromoalkanes, on the assumption that substituent interactions can be transmitted along the chain and also through space.

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 12, pp. 2770-2776, December, 1988. Original article submitted July 21, 1987. In view of the above discussion, the topological scheme used to describe the change in CS of carbon due to replacement of a hydrogen atom in the molecule by a heteroatom must start with the CS of this C atom in the isostructural hydrocarbon [7] and must take into account the influence of the complete heterograph in the form of a sum of increments of one-particle and two-particle heterosubgraphs and the interaction of the latter with neighboring hydrogen atoms.

It is natural to base the description of 13 C NMR spectra on numerical topological characteristics of a plane carbon graph of the molecule, consisting of a graph of the isostructural hydrocarbon and a heterograph indicating the positions of the substituents. In this way we select the orders of the



vertices s_j (number of C-C bonds in which each C_j participates); $p_{1,i-1}$ is the number of oneparticle heterosubgraphs G_1 with a distance of i bonds between the heterosubstituent and the given C_0 ; $p_{k,i-1}$ is the number of two-particle heterosubgraphs G_k pertaining to each one-particle subgraph; the heterosubgraph G_k element closest to the C_0 under consideration is separated from this C_0 by i bonds.

As the topological element for increment schemes of $\delta^{-13}C$ in polyhalomethanes, it was proposed for the first time in [4] to examine not the X atom, but rather the C-X bond through which the influence of the X itself and its steric interactions with the other substituents is transmitted to the C atom. It was found that the increment of the bond $\Delta\delta$ C-X in the molecule CX_mH_{4-m} varies quadratically with the number m - 1 (in our notation, p_{2,0}) of two-particle interactions in which each substituent X participates.

As investigation of ¹³C NMR spectra of polyiodoalkanes [5] showed that the CS of iodinesubstituted C atoms can be described by using the bond increment $\Delta\delta$ C-I, in which nonvalence two-particle interactions of the particular iodine atom with all others are summed and expressed by a quadratic dependence on the numbers $p_{k,0}$

$$\Delta\delta (C-I) = B_0 + B_2 p_{2,0}^2 + B_3 p_{3,0}^2 + B_4 p_{4,0}^2 - \dots,$$
(1)

where B_0 is a constant corresponding to the true α -effect of the substituent in the monosubstituted methane CH_3X ; B_k are the increments of the indexes $p_{k,0}$, which depend on the properties of the substituent and can be determined experimentally.

In a study of branched monoiodoalkanes [6] it was shown that there are no grounds for the view generally held for increment schemes, the view that a substituent makes a constant contribution to the CS of the carbon atom (α -, β -, and γ -effects). Thus, the α -effect of the iodine atom contains the constant B₀ and depends both on the order of the vertex C_{α} (s_{α}) and on the total number of hydrogen atoms on all C_{β}; the β -effect of iodine correlates with the number of hydrogen atoms on the given C_{β}.

In calculating $\delta^{13}C_j$ (j = 1, ..., n) for each j, the carbon graph of the substituted alkane is represented as a tree with root $C_j = C_0$ and branches with various lengths, such that the influence of substituents can be examined after distributing them on circles with radius i (i = 1, 2, 3):



With i \leq 3, three types of relative location of two substituents are possible (assuming that bromine atoms that are farther apart from each other will affect the CS of carbon atoms independently. These types are geminal, vicinal, and 1,3-pairs of heteroatoms:



The increment of each G_k in $\delta^{13}C_0$ will be denoted by the symbol $\Gamma_{k,i-1}$, where the subscript i-1 indicates how many bonds intervene between the closest element of the heterosubgraph G_k and C_0 .

It was found in [6], however, that the increments of steric interaction of substituents $\Gamma_{k,i-1}$ give a good description of the CS of carbon only in those compounds in which the C atoms have either an identical degree of substitution by heteroatoms, or zero substitution. Otherwise, it is necessary to introduce an additional increment A_k to account for asymmetry of the bundle GA_k of two-particle heterosubgraphs G_k with respect to the substitued C_0 on one of the ends of GA_k (k > 1). We will define the asymmetry index as

$$a_k = p_{1,0} - p_{1, k} 2 \tag{2}$$

this quantity being equal to the difference between the numbers of heterosubstituents on C_0 and C_{k-2} , which is the second substituted node of the bundle GA_k . An example (* = C_0):

$$X X X X (GA_3): a_3 = p_{1, 0} - p_{1, 1} = 3 - 1 = 2;$$

$$X X X X (GA_3): a_3 = p_{1, 0} - p_{1, 1} = 1 - 3 = -2$$

This influence on $\delta^{13}C_0$ (increment A_k) was found to decrease sharply with increasing k, so that it has essentially zero magnitude with k > 4.

All of the above-examined contributions of substituents can be combined into the sought equation for the CS of carbon atoms $C_0 = C_j$ (j = 1, ..., n)

$$\delta^{13}C_{0} = \delta^{13}C_{H} + p_{1,0}\left(\Gamma_{1,0} + \sum_{k=2}^{4} p_{k,0}\Gamma_{k,0}\right) + \sum_{k=2}^{5_{0}} p_{1,1}\left(\Gamma_{1,1} + \sum_{k=2}^{4} p_{k,1}\Gamma_{k,1}\right) + \sum_{1}^{5_{0}}\sum_{1}^{5_{1}} p_{1,2}\left(\Gamma_{1,2} + \sum_{k=2}^{4} p_{k,2}\Gamma_{k,2}\right) + \sum_{k=3}^{4} p_{1,0}p_{1,k-2}a_{k}A_{k}$$

$$(3)$$

In Eq. (3), $\delta^{13}C_H$ is the CS of the C₀ atom in the isostructural hydrocarbon; the second, third, and fourth terms describe (respectively) the α -, β -, and γ -effects of the elementary heterosubgraphs on $\delta^{13}C_0$; the last term characterizes the symmetry of the heterograph in the vicinity of C₀ within the limits of three bonds; $p_{k,i-1}$ (i = 1, 2, 3) and a_k are the numbers of increments of a given type: $\Gamma_{k,i-1}$ and A_k . The form of the terms in Eq. (3) was selected so that if any structural element is absent from the molecule ($p_{k,i-1} = 0$ or $a_k = 0$), the corresponding term of Eq. (3) will vanish.

Our problem is to find the unknown increments $\Gamma_{k,i-1}$ and A_k by solving the inverse problem of multiparameter linear regression given by the system of Eq. (3) with experimental values of δ ¹³C in the left-hand side. In view of the dependence of the increments $\Gamma_{k,i-1}$ on the structure of the carbon skeleton around C_0 , we will seek the increments in the form of additive functions of the simplest topological indexes: the orders of the vertices of the carbon atoms in the immediate vicinity of C_0 (s_0 , s_1 , and s_2), the number of hydrogen atoms h_0 on C_0 itself, and the number of hydrogen atoms h_1 in the β -vicinity of $C_0 - i.e.$, the sum over all C_1 . The indexes h_0 and h_1 , although they are not linearly independent topological parameters, indicate the presence of real steric interactions between heteroatoms and the neighboring hydrogen atoms; and hence they must be represented by their coefficients in the increments $\Gamma_{k,i-1}$.

The inverse problem of multiparameter linear regression consists of finding the solution of a system of linear equations of the type (3), the number of equations being equal to the number of experimental values of $\delta^{13}C_0$ for polybromoalkanes that were taken in the calculation; and the database of variables forms the sought coefficients of the topological indexes. A solution of this problem by the least squares method is unstable relative to variations of the parameters (for example, the natural error in determining $\delta^{13}C_0$ under various conditions), and it cannot be regarded as an approximate solution of the problem, since small errors of measurement may lead to indeterminately large errors in the sought increments. In order to find an approximate normal solution, it is necessary to bring in the method of regularization of incorrectly posed inverse problems [8] with an estimate of accuracy [9] of the selected approximation.

<u></u>		δ, PI	om fron	1 TMS (and δ_e	xp ^{-δ}	Lit.		
Compound		C:	C:	C3	C1	C ⁵	C6	C7	ref.
CH₂BrCH₂Br	(I)	29,2	29.2						
CHBr ₂ CHBr ₂	(II)	(-0,9) 47.2	(-0,9) 47,2						
CHBr ₂ CH ₂ CHBr ₂	(III)	(0,6) 40,7	(0,6) 57,3	40.7					[10]
CH₂BrCHBrCH₂Br	(IV)	(-0,7) 35,4	(0,5) 48,9	(-0,7) 35,4					
CHBr ₂ CHBrCH ₂ Br	(V)	(-0,2) 45,9	(1,3) 57,4	(-0,2) 34.2					[3]
CH2BrCH2CHBrCH3	(VI)	(0,4) 30,6	(-1,4) 43,2	(-0,7) 47,6	26,1				[3]
CHBr ₂ CH ₂ CHBrCH ₃	(VII)	(0,7) 43,1	(-0,2) 55,1	$\begin{vmatrix} (-2,1) \\ 47,0 \end{vmatrix}$	(0,9) 25,8				[11]
CBr _s CH ₂ CHBrCH ₃	(VIII)	(-0,9) 36.1	(-0,1) 67,4	(0,2) 45.2	(0,3) 27,4				[11]
CHBr ₂ CH ₂ CBr ₂ CH ₃	(IX)	(0,9) 38,0	(1,4) 64,8	(0,7) 61,8	(0,2) 41,0				
CHBr ₂ CHCH ₂ Br	(X)	(1,5) 50,2 (-2,2)	(0,1) 46,0 (0,8)	(-0,6) 34,8 (0,5)	(-1,4) 15,8 (0,5)				[12]
CBr ₂ (CH ₂ CH ₂ Br) ₂	(XI)	68,4	53,2	26,7					
CH2BrCH2CHBrCH2CHBrCH3	(XII)	30,2	$\begin{array}{c} (2,1) \\ 40,1 \\ (0,4) \end{array}$	53,3	48,6	46,0	24,9		[13]
CH2BrCHBrCH2CH2CH2CH2CH3	(XIII)	(-0,7) 35,7 (-0.8)	$\begin{array}{c} 40,1 \\ (-1,0) \\ 52,4 \\ (0,3) \end{array}$	(-0,8) 35,7 (0,9)	(-1,1) (-1,0)	$ \begin{array}{c} 51,0\\(-1,5)\\30,9\\(0,3)\end{array} $	(-0,8) 22,4	14,0	
CHBr ₂ CH ₂ CHBrCH ₂ CH ₂ CH ₂ CH ₃	(XIV)	43,5	54,1	53,3	38,0	29,2	21,9	13,9	[11]
CHBr2CH2CHCH2CHBrCH3 i CH3(7)	(XV)	43,7 43,8 (0,3)	52,5 51,6	31,2 31,3 (1.0)	47,2 48,3	47,6	26,2 26,9	17,8 18,5	[12]
CHBr ₂ CH ₂ CHBrCH ₂ CHBrCH ₂ CH ₃	(XVI)	(0.3) 42.7	52,9	(1,0) 52,6	(-0,7) 46,7	(-0,6) 56,3	(1,2) 32,2	11,9	[1]
CHBr ₂ CH ₂ CHBrCH ₂ CH ₂ CHBrCH ₃	(XVII)	$\begin{array}{c} (-0.7) \\ 42.9 \\ 42.8 \end{array}$	(-1,0) 53,4 53,2	(-0.8) 52,8	(-1,0) 36.7 36.2	(-1,5) 38,7 38,1	(-0,8) 50,0 49.7	26,4	[1]
CBr ₃ CH ₂ CHBrCH ₂ CH ₂ CH ₂ CH ₃	(XVIII)	(0.9) 36.5	(1.0) 66,8	$^{(-0,3)}_{51.7}$	(-0,2) 39,2	(0.5) 29,5	(-0.8) 21,8	(1.2) 14,1	[11]
CBr ₂ (CH ₂ CHBrCH ₃) ₂	(XIX)	(0,8) 68,5	(-0,8) 59,9	(0,6) 45.3	(0,2) 27,9	(0,0)			
CBr ₂ CH ₂ CHBrCH ₂ CH ₂ CH ₂ CH ₃	(XX)	(0,9) 69.2 69.2	$ \begin{array}{c} 60,0 \\ (-0,9) \\ 59,3 \end{array} $	45,4 (-1,2) 52.0	$\begin{array}{c} 28,1 \\ (-1,8) \\ 39,8 \\ 39,9 \end{array}$	29,3	21,8	13,9	[14]
│ CH₂CHBrCH₃		(1,7)	(1.0) 60,2	(-0,5) 45,5 45.6	(0,6) 27.9 28.1	(-0,2)			
CBr ₂ (CH ₂ CHBrCH ₂ CH ₂ CH ₂ CH ₃) ₂	(XXI)	69,6 (1,7)	(-0,7) 59,3 (1,0)	(-1,0) 52,0 (-0,5)	(-1,8) 39,8 (0,7)	29,3 (-0,3)	21,3	13,9	[14]

TABLE 1. Values of ^{13}C NMR CS in Polybromoalkanes, and Deviations from Values Calculated Using Eq. (3)

In determining the empirical dependence of the ¹³C CS in polybromoalkanes on their topology, we have studied the ¹³C NMR spectra of 35 compounds, some of which have been described previously [3, 4] (Table 1). In addition, we made use of data on the ¹³C NMR spectra of 13 monobromoalkanes [15, 16]. The initial database for calculation consisted of 107 equations of the type (3) for 33 linear regression parameters. Some of the coefficients proved to be equal to zero, so that we were subsequently able to cut the number of unknowns in Eq. (3) to 27. In certain cases, the error in reproducing the experimental values of the CS (δ ¹³C_{exp} - δ ¹³C_{calc}) was considerably above the allowable level, amounting to 3 ppm. In order to determine the reasons for this, we removed from the calculation database the data for compounds (X) and (XI), in which these carbon atoms appeared, and also compounds of similar structure (VI), (XIX), (XX), and (XXI), as well as compounds with side-by-side location of Br atoms (IV) and (V). The remaining database consisted of a system of 93 equations with 27 unknowns; the nonzero solutions of this system are listed in Table 2, along with the confidence intervals of the least squares method for each coefficient.

The standard error in reproducing the 13 C NMR CS in polybromoalkanes according to Eq. (3) with the coefficients of Table 2 is 0.99 ppm at the 95% level; this error cannot be

Topologi- cal ele- ments G_k and GA_k	Relative positions of G_k and GA_k , and $C_0(\bullet)$	Increments $\Gamma_{k,i-1}$ and a_k , and con- fidence intervals of coefficients of topological indexes ^a	Frequencies of indexes
Gı	X *	$ \Gamma_{1,0} = (11,76\pm0,04) + (6,04\pm0,06) s_0 + + (0,84\pm0,10) h_1 $	43: 39; 38
	X *	$\Gamma_{1,1} = (1,40\pm0,02) s_0 + (3,33\pm0,007) h_0$	45: 44
	X *	$\Gamma_{1,2} = (-0.95 \pm 0.17) + (-1.15 \pm 0.51) s_1 + + (0.55 \pm 0.05) s_2$	37: 38; 36
G2	X X	$ \Gamma_{2,0} = (-2,08\pm0.08) p_{2,0} + (1.89\pm \pm 0,08) s_0 + (-1,38\pm0.26) h_1 $	17: 16; 14
	$X \searrow . \underline{\swarrow X}_*$	$\Gamma_{2,1} = (-0.67 \pm 0.08) s_0 + (1.07 \pm 0.11) h_0$	20: 22
	X X	$\Gamma_{2,2} = (0,45 \pm 0,13) s_2$	13
G3	X X X	$ \Gamma_{3,0} = (6,82\pm0,19) p_{2,0} + (-3,94\pm \pm 0,20) p_{3,0} $	3: 8
G4	X X	$\Gamma_{4,0} = (-0.60 \pm 0.14) p_{4,0}$	18
	X X	$\Gamma_{4,-1} = (-0,28\pm0,08) h_0^{b}$	17
	X X	$\Gamma_{4,1} = (-0,32\pm0,11) s_1 + (0,40\pm0,24) h_0$	16; 17
	X X	$\Gamma_{4,2} = (-0,40\pm0,11) s_2 + (0,30\pm0,55) h_0$	9: 9
GA3	X X X ·	$A_3 = (-5,31 \pm 0,50); a_3 = p_{1,0} - p_{1,1}$	4
GA4	X X X	A ₁ = $(-0.58\pm0.15); a_4 = p_{1,0} - p_{1,2}$	9

TABLE 2. Coefficients in Eq. (3) for Empirical Estimation of $\delta^{13}C_0$ in Polybromoalkanes

^aTopological elements for which zero linear regression coefficients were obtained are omitted from this table. ^bFor C atom with G_4 , i = 0.

reduced by changing the topological variables in the increments. We can distinguish four main sources of error: 1) the statistical justification of each index; 2) the selection of indexes for each increment $\Gamma_{k,i-1}$; 3) the three-bond limitation on the influence of the environment of the C atom on the value of δ^{13} C; 4) the limits of applicability of the plane graph model.

As can be seen from Table 2, the topological indexes are represented satisfactorily in the database, and they do not reveal any direct link between the frequency and error of the coefficient for a particular index. The selection of the form of the increments $\Gamma_{k,i-1}$ is governed by earlier studies [4-6] and is supported by the fact that the principal increments $\Gamma_{k,0}$ have small confidence intervals. For the other increments, therefore, a similar dependence on the topological indexes has been selected. An exception is the form of the increment $\Gamma_{1,2}$, which represents the γ -effect of the Br atom and has no analogy with the iodoalkanes [4, 5], since the γ -effect of iodine is very small and not amenable to topological analysis. This question may be clarified in the future through studies of chlorine and fluorine derivatives.

Attenuation of the influence of the Br atom beyond the three-bond limit can be seen in the example of $\delta^{13}C$ for the C atoms belonging to the alkyl chains of the compounds listed in Table 1.

The main source of error is apparently the plane molecular graph model itself, the model on which all topological increment schemes for the physical properties of molecules have been based. As can be seen from Table 2, almost all the increments relate to steric interactions of heteroatoms with each other or with hydrogen and carbon atoms of the nearest part of the skeleton. These quantities depend on the interatomic distances; and a plane graph cannot account for changes due to conformational conversion of nonrigid molecules. As a result, the relative error of the coefficients (Table 2) increases with increasing k and with increasing number of bonds (i - 1) between C_0 and G_k . For example, the error in determining the first two coefficients of $\Gamma_{1,0}$ is no greater than 1%, but the error increases to 12% for the coefficient of h_1 - the total number of hydrogen atoms on all C_1 . In actual fact, not all of the indicated hydrogen atoms participate in steric interactions with Br atoms connected to C_0 , since internal rotation takes place around all C_0 - C_1 bonds. Thus, for G_2 , with increasing removal of C_0 from geminally bonded Br atoms, the error increases from 4% to 30%; and for G_4 , the error of the coefficients increases from 20% to 180% with increasing i.

On the other hand, according to the data of Table 2, the main contribution to $\delta^{-13}C_0$ is made by only a few increments with adequately small confidence intervals. With increases in the parameters k and i, the coefficients of the topological indexes decrease sharply; moreover, they may enter into the expressions for the increments (for example, $\Gamma_{4,1}$ and $\Gamma_{4,2}$) with different signs, thus having little overall effect on the estimate of $\delta^{-13}C_0$ as determined by Eq. (3).

Calculations of the CS of C atoms in polybromoalkanes by the proposed scheme (Table 1) are in satisfactory agreement with experiment, with certain exceptions that are not always random occurrences. Attention is drawn to 1,3,3,5-tetrabromopentane (XI) and compounds (XIX)-(XXI), for which the complete heterographs are identical. In these compounds we observe two systems of errors: deviation of $\pm(2-3)$ ppm for all C atoms of (XI), and a positive error as great as 1.7 ppm for the CS of the CBr₂ carbon in (XIX)-(XXI), in contrast to the other C atoms of these latter compounds, for which the deviations of the calculated values of δ^{13} C meet the standard that has been obtained (0.99 ppm). The second error can be eliminated quite easily if we assume that for the central node of the complete heterograph, the influence of the bundles of the heterosubgraphs GA_k (in this case, CBr_2 and GA_4) should be regarded as a difference rather than a sum, since the directions from the central geminal pair to the peripheral isolated Br atoms are opposite to each other. This means that the increments A_k describe the mutual inductive influence of substituents, transmitted through the molecular skeleton. The error for CBr_2 in this case amounts to -0.6, -0.2, and -0.2 in (XIX), (XX), and (XXI), respectively; but for the same C atom in (XI), the error increases to -4.6 ppm.

Such a sharp difference between the experimental and calculated values of δ^{-13} C in compound (XI) may be explained on the basis that in this compound, for the C₁-C₂ and C₄-C₅ bonds, a single conformation, with fixed distances between atoms, predominates. The plane graph model does not account for differences in interatomic distances; and that particular part of the solution of the inverse multiparameter regression problem which describes the influence on δ^{-13} C from nonvalence interactions of heteroatoms in different fragments implies interatomic distances that are averaged over the entire database for the substances studied. Correspondingly, the best estimates of the CS should be obtained for compounds with a large set of conformations that are similar in energy.

EXPERIMENTAL

The ¹³C NMR spectra were obtained in a Bruker WP-200 SY Fourier transform spectrometer (50.31 MHz) in the "Jmodecho" mode without any noise decoupling with respect to protons, operating on 30% solutions in CCl₄ (95.99 ppm from TMS) or CHCl₃ (77.17 ppm from TMS).

Syntheses of the compounds (Table 1) have been described previously [1, 11, 13, 14, 17]. Compound (XIII) was obtained by bromination of 1-heptene by a procedure given in [10].

<u>1,3-Dibromobutane (VI)</u>. A mixture of 10 mmoles of (VII), 10 mmoles of trimethylsilane, and 1 mmole of $Fe(CO)_5$ was heated in a sealed glass ampul for 4 h at 130°C; iron salts and tar were removed by passing through a bed of silica gel, and the product was distilled. From the 48-90°C fraction (12-14 mm), by preparative gas chromatography, (VI) was obtained in 18% yield, n_D^{20} 1.5090, d_4^{20} 1.7953. Found, %: C 22.39, H 3.83, Br 73.76, MR 35.9, $C_4H_8Br_2$. Calculated, %: C 22.25, H 3.73, Br 74.02, MR 36.2.

<u>1,1,3,3-Tetrabromobutane (IX)</u>. A mixture of 26.4 mmoles of $CHBr_3$, 13.2 mmoles 2-bromopropene, 1.3 mmoles $Fe(CO)_5$, and 4 mmoles DMFC was heated for 4 h at 100°C in a glass ampul; the reaction mixture was diluted with two volumes of hexane and passed through a bed of silica gel (1 × 3 cm), after which it was distilled. recovering (IX) in 39% yield relative to the CHBr₃ reacted (CHBr₃ conversion 45%); bp 85°C (2 mm), n_D^{20} 1.5920, d₄²⁰ 2.4327. Found, %: C 13.08, H 1.63, Br 85.08, MR 51.99, C₄H₆Br₄. Calculated, %: C 12.85, H 1.62, Br 85.53, MR 51.73.

CONCLUSIONS

1. For the first time, an empirical scheme has been proposed for estimating the chemical shift of carbon atoms in polybromoalkanes (including bromomethanes) with an error of ± 1 ppm — a scheme based on the simplest topological indicators of a molecular graph and readily accessible algorithmization.

2. It has been shown that the plane graph model gives the best agreement between calculated and experimental values of the chemical shift of carbon atoms in the case of polysubstituted alkanes with a large number of equally probably conformations.

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