STRUCTURAL INCREMENTS OF ^{13}C NMR CHEMICAL SHIFTS IN MONOIODOALKANES

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In establishing the structure of halooorganic compounds by means of ^{13}C NMR spectra, increment schemes for calculating ^{13}C NMR chemical shifts (CSs) play an important role [1, 2]. It is necessary to determine the general relationships governing the action of the heteroatom on the hydrocarbon skeleton of the molecule, action that is responsible for the change in CS of the α-, β-, and γ-carbon atoms in comparison with the isostructural hydrocarbon.

In this sense, monoiodoalkanes can serve as a convenient object of investigation. Because of the large volume of the iodine atom and the fact that it is readily polarized, its interaction with the skeleton of the molecule is manifested in ^{13}C NMR spectra so distinctly that it is possible to distinguish the individual, specific elements. No such systematization has yet been performed on ^{13}C NMR data for iodoaliphatic comounds, although approaches to the problem have been worked out in [3-5].

In the present work, within the framework of a structural approach that we have developed, we have also systematized the literature data on the ^{13}C NMR chemical shifts of monoiodoalkanes (Table 1).

The ^{13}C NMR chemical shifts in the monoiodoalkanes occupy an interval from −24 ppm for CH_3I to +72 ppm for $IC(C_2H_5)_3$; this is evidence of the high sensitivity of the CS of the carbon carrying the iodine to its structural environment. As shown by the data of Table 1, the signals of the CH_2I group occupy the region from −1.5 to +9 ppm, and the value of $\delta^{13}C_\alpha$ for 1-iodoalkanes with a normal hydrocarbon chain longer than three C atoms is also approximately 6 ppm. The $-CHI-$ grouping, under the influence of two alkyl substituents, gives $^{13}C_\alpha$ signals in the weaker field: 21-44 ppm, with an average value of approximately 39 ppm for normal secondary iodoalkanes. The two examples in which the iodine atom is positioned on a tertiary C atom (compounds VIII and XVI in Table 1) show that the trend toward a downfield shift of the C_α signal is maintained as the length of the hydrocarbon substituent is increased. We can assume that for normal alkyl substituents R, the range of variation of $\delta^{13}C_\alpha$ for ICR_3 is 43-72 ppm; with increasing length of the alkyl substituent, $\delta^{13}C_\alpha$ will tend toward a value of approximately 65 ppm. These evaluations show that the signals of the iodine-containing groupings $-CH_2I$, $-CHI$, and $CI-$ have very little overlap with each other; they are readily identified in the ^{13}C NMR spectra, and they can serve for preliminary determinations of structure and identification of products from reactions of iodoaliphatic comopunds.

A simple comparison of the ^{13}C CS for even a small number of iodoaliphatic compounds indicates the existence of several types of interaction of iodine with its surroundings, interactions that are comparable in magnitude and different in nature. In [3], for example, it was noted for the first time that the α- , β-, and γ-increments of iodine in $\delta^{13}C$ vary with the position of the iodine in the molecular chain. It was found in [4] that in monoiodoalkanes, the CSs of the α-, β-, and γ-carbon atoms are linearly related to the CSs of the corresponding C atoms in the isostructural alkanes. A factor analysis of the ^{13}C NMR chemical shifts in various monohalides [5] showed that the influence of the halogen atom on $\delta^{13}C_{\alpha,\beta,\gamma}$ is determined by three basic factors: the polar properties of the Hal atom replacing the hydrogen, the lability of the electron pairs of the Hal, and some factor that was not determined in [5] − a factor affecting mainly C_α. It was also noted in [6] that the medium influences the ^{13}C NMR signals in monoiodoalkanes.

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TABLE 1. ^{13}C NMR Chemical Shifts in Monoiodoalkanes

Compound	Formula (and solvent)	^{13}C Chemical shift, ppm, from					
		C^1	C^2	C^3	C^4	C^5	C^6
(I) *	ICH_3	−23,5					
	(C_6H_{12})	−24,5					
(II)	$ICH_2CH_3(CDCl_3)$ [4]	−1,5	20,6				
(III)	$ICH_2CH_2CH_3(CDCl_3)$ [4]	9,1	27,0	15.3			
(IV)	$ICH(CH_3)_2(CDCl_3)$ [4]	21,0	31.2				
	(without solvent) [6]	20,2					
	(C_6H_{12}) [6]	16,9					
	(CH_3NO_2) [6]	22,4					
(V) *	$ICH_2CH_2CH_2CH_3$	6,1	35,5	23,6	13,1		
	$(CDCl_3)$ [4]	6,4	35.6	23.7	12,9		
(VI)	$CH_3CHICH_2CH_3(CDCl_3)$ [4]	28,5	32.2	36,0	14.2		
(VI) *		28,2	31,9	35,6	13,9		
(VII)	$ICH_2CH_2CH(CH_3)_2(CDCl_3)$ [5]	4.4	42.7	29,1	21,7		
(VIII)	$IC(CH_3)_3$ [5]	43.0	40.4				
(IX) *	$ICH_2CH_2CH_2CH_2CH_3$	6,2	33,2	32,6	21,6	14,0	
(X)	$CH_3CHICH_2CH_2CH_3(CDCl_3)$ [4]	28,9	29,4	45,0	22,9	13,1	
(XI)	$ICH(CH_2CH_3)_2$ [5]	43,9	33,2	13,9			
	$(CDCl_3)$ [4]	44,2	33,4	14,1			
(XII)	$CH_3CH_2CHICH_2CH_2CH_3(CDCl_3)$ [5]	14,1	33,8	41,7	42,4	22,8	13,2
(XIII) *	$CH_3CHICH_2CH_2CH_2CH_2CH_3$ †	28,7	29,3	42,7	29.4	28,2	31.4
(XIV) *	$CH_3CH_2CHICH_2CH_2CH_2CH_3$ †	13,8	33.3	41,1	39,6	31.3	21,6
(XV) *	$ICH(CH_2CH_2CH_3)_2$	38,5	42,4	22,4	13,0		
(XVI)	$IC(CH_2CH_3)_3$ [5]	71,6	36,7	11,3			
(XVII) *	$CH_3CHICH_2CH_2CH_2CH_2CH_2CH_3$ †	28,7	29,3	42,7	29,4	28,2	31,4
(XVIII)	$CH_3CH_2CHICH_2CH_2CH_2CH_2CH_3$ †	13,7	33.4	40,8	40.1	39,9	30.7

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*Determined for 60% solutions in $CHCl_3$.

†(XIII) 7-CH_3 13.8; (XVII) 7-CH_2 22.3, 8-CH_3 13.8; (XIV) 7-CH_3 13.8; (XVIII) 7-CH_2 22.4, 8-CH_3 13.7 ppm.

TABLE 2. α-Effect of Iodine in $\delta^{13}C$ of Monoiodoalkanes: $\alpha_I = \delta^{13}C_{\alpha RI} - \delta^{13}C_{RH}$

Compound	$\delta_{CRI,\alpha}$	$\delta_{CRH,\alpha}$ [5]	α_I	n_C	n_H
(I)	−24,0	−2,1	−22,0	0	0
(II)	−1.5	6.5	−8,0	1	3
(IV)	21,0	16.3	4.7	2	6
(VIII)	43.0	23,3	19,7	3	9
(XI)	44,1	34,2	9,9	2	4
(XII)	41.7	31,7 [7]	10.0	2	4

Note. $\delta C_{RH,\alpha}$ is the CS of the α-C atom in the alkane RH that is isostructural with the particular iodoalkane RI; n_C is the number of β-C atoms (relative to the position of the iodine atom); n_H is the number of protons vicinal with respect to the iodine atom.

The present work has been aimed at developing an empirical additive scheme for the calculation of $\delta^{13}C$ in monoiodoalkanes with various types of structure. As can be seen from the data for compound (IV) in Table 1, the CS of C_α in 2-iodopropane varies with the solvent within the interval 16.9-22.4 ppm, the closest agreement being observed between results obtained for the pure substances and its solution in $CHCl_3$ ($CDCl_3$). Data reported in [2, 3, 5] indicate that this effect also occurs for other monohaloalkanes. In this connection, the increment scheme is preferably based on data obtained for a solution in $CHCl_3$, considering that the error of 1.5-2 ppm is unavoidable in view of the strong action of the solvent on the C—I bond.

In order to determine the factors governing the α-effect of iodine in monoiodoalkanes, let us compare the change in the C_α CS in certain simple molecules (Table 2). It can be seen that the α-effect of iodine, traditionally defined as the difference in C_α CS in substituted and unsubstituted alkanes, varies over broad limits, manifesting a definite dependence on the number of C_β atoms connected to the iodine-containing atom C_α and also on the number of

TABLE 3. Increments of α-, β-, and γ-Effects of Iodine in Monoiodoalkanes for (1) and (2): $\Delta C_i = \delta C_{RI,\,i} - \delta C_{RE,i} = A_{0,i} + A_{C,i}\, n_C + A_{H,i}\, n_H^i$, $i = \alpha,\ \beta,\ \gamma$*

Effect	A_0	A_C	A_H	No. of experimental values (N)
α	−23.3	22,6	−2,8	18
β	0.7	0,6	4,5	25
γ	−1,2	0.5	0,2	12

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*In the case of the α-effect, n_H^α is the sum of all vicinal protons; for the β- and γ-effects, n_H^i is the number of protons on C_β or C_γ, respectively; n_C is the number of β-carbon atoms with respect to the position of the iodine atom.

hydrogen atoms H_β on all C_β in the vicinity of the iodine atom. As a matter of fact, in compounds (XI) and (XII) (Table 2), which are identical in terms of numbers of C_β and H_β, the α-effect of iodine is constant. In this connection, for our statistical analysis of C_α CS in all of the monoiodoalkanes we have investigated (see Table 1), we selected the following two-parameter linear regression equation:

$$\delta^{13}C = \delta^{13}C_{RH,\,\alpha} + \alpha_I = \delta^{13}C_{RH,\,\alpha} + A_{0,\,\alpha} + A_{C,\,\alpha} n_C + A_{H,\,\alpha} n_H \qquad (1)$$

where $\delta^{13}C_{RH}$ is the CS of the corresponding carbon atom in the isostructural alkane; n_C is the number of C_β atoms; n_H is the number of hydrogen atoms that are vicinal with respect to the iodine atom under consideration.

The constant A_0, according to (1), determines the change in $\delta^{13}C$ in CH_4 when one hydrogen atom is replaced by an iodine atom (when $n_C = n_H = 0$):

$$A_0 = \delta^{13}CH_3I - \delta^{13}CH_4$$

The constant should be termed the true α-effect of iodine, which is independent of structural factors. The magnitude of A_0, as found on the basis of (1) for a large body of experimental data on $\delta^{13}C_\alpha$, enables us to eliminate possible errors in the measurements of $\delta^{13}CH_3I$ and $\delta^{13}CH_4$.

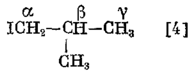
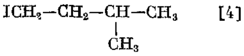
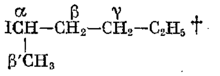
The dependences of $\delta^{13}C_\beta$ and $\delta^{13}C_\gamma$ are best represented by equations analogous to (1), here, the parameters n_H^i should reflect the number of hydrogen atoms for the particular C_β or C_γ participating in steric interaction with the iodine atom, and the parameter n_C, the same as previously, is equal to the number of carbon atoms in the β-position relative to the iodine atom (i.e., the degree of branching of C_α):

$$\delta^{13}C_i = \delta^{13}C_{RH,\,i} + A_{0,\,i} + A_{C,\,i} n_C + A_{H,\,i} n_H^{\,i}; \qquad i = \beta,\ \gamma \qquad (2)$$

In Table 3 we have listed values of the coefficients in (1) and (2), and also the number of experimental values of $\delta^{13}C_{\alpha,\beta,\gamma}$, that were used in finding these coefficients by the least-squares method. As shown by the values of $A_{H,\alpha}$ and $A_{H,\beta}$, steric interactions of iodine with vicinal protons make a substantial contribution to $\delta^{13}C_\alpha$ and $\delta^{13}C_\beta$. The α-effective iodine, moreover, has two components that are extremely large and are opposite in sign. One of them, A_0, is negative; it is possible, therefore, that the true α-effect of iodine is determined by the steric properties of iodine to a greater degree than by its electronegativity. For chlorine and bromine, on the other hand, the main factor determining the true α-effects is apparently the electronegativity of the Hal atom, since $A_{0,\alpha}(Cl)$ and $A_{0,\alpha}(Br)$ are positive [8].

Attention is drawn to the large positive value of $A_{C,\alpha}$, which determines the fraction of $\delta^{13}C_\alpha$ pertaining to each carbon atom in the β-position relative to the iodine atom, or,

TABLE 4. Examples of Calculation of ^{13}C NMR Chemical Shifts for Certain Monoiodoalkanes on the Basis of (1) and (2) (values of δ_H, other than those for (IX), were taken from [7])

Compound	Formula	^{13}C CS (exp/calc), ppm from TMS		
		C_α	C_β	C_γ
(XIX)	 $\overset{\alpha}{I CH_2}-\underset{CH_3}{\overset{\beta}{CH}}-\overset{\gamma}{CH_3}$ [4]	$\frac{18.0}{21.4}$	$\frac{30.6}{29.1}$	$\frac{22.6}{24.5}$
(XX)	$ICH_2-CH_2-CH_2-C_2H_5$ [6] *	$\frac{5.9}{7.2}$	$\frac{33.2}{32.5}$	$\frac{32.5}{33.8}$
(XXI)	 $ICH_2-CH_2-\underset{CH_3}{CH}-CH_3$ [4]	$\frac{4.4}{5.2}$	$\frac{42.7}{41.9}$	$\frac{29.1}{29.4}$
(XXII)	 $\underset{\beta' CH_3}{\overset{\alpha}{ICH}}-\overset{\beta}{CH_2}-\overset{\gamma}{CH_2}-C_2H_5$ † [4]	$\frac{30.2}{30.6}$	$\frac{42.7}{42.6}$	$\frac{31.9}{31.9}$

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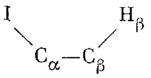
*CSs were recalculated to TMS from CS_2.
†For $C_{\beta'}$, 28.9/29.1.

which is the same thing, the fraction pertaining to each carbon chain attached to C_α. All α-, β-, and γ-contributions of carbon atoms contained in these chains have already been taken into account in (1) through the original value of $\delta^{13}C_{RH,\alpha}$, such that the increase in $\delta^{13}\ C_\alpha$ by an amount $A_{C,\alpha}n_C$ is related to the very fact of existence of these chains, n_C in number. The source of this phenomenon may be than an α-branched alkyl chain is more susceptible than a normal chain to the inductive effect of iodine. This is also responsible for the broad range of variation of the α-effect of iodine (∿42 ppm; see Table 2) with variation of the molecular structure.

The constant components of the β- and γ-effects, $A_{0,\beta}$ and $A_{0,\gamma}$, are considerably smaller in absolute magnitude than $A_{0,\alpha}$; this is consistent with rapid attenuation of the inductive effect of a substituent along the chain. As can be seen from Table 3, the coefficients $A_{C,\beta}$ and $A_{C,\gamma}$ in (2) are small, i.e., the β- and γ-effects of iodine have very little dependence on the structure of the molecule at the point C_α.

With regard to the β-effect, it is indicative that all three coefficients of (2) are positive, such that the introduction of an iodine atom into the molecule always leads to a downfield shift of the signals of carbon atoms adjacent to the iodine-containing carbon atom, an effect analogous to that of Cl and Br. The contribution of steric interaction of iodine with the hydrogen atoms in $\delta^{13}C_\beta(A_H,\ _\beta n_H)$ has the same sign as the constant component of the β-effect $A_{0,\beta}$, but is considerably greater (particularly in the case of two or three H_β). This shows that the steric part of the β-effect of iodine is decisive in comparison with the inductive part.

A comparison of $A_{H,\alpha}$ and $A_{H,\beta}$ shows that steric interaction of iodine with H_β protons leads to a decrease in δC_α but an increase in δC_β. It is interesting that the increments $A_{H,\alpha}$ and $A_{H,\beta}$, which are opposite in sign, are very similar in absolute magnitude. Actually, one and the same proton H_β participates in determining δC_α and δC_β [Eqs. (1) and (2)]



such that the conformation-averaged steric interaction I–H is transmitted to C_β through only one bond $H_\beta-C_\beta$, but it is transmitted to C_α through two bonds H_β-C_β and C_β-C_α; this may be the reason for the alternation of sign of these coefficients, and also the certain decrease in absolute $A_{H,\alpha}$.

The γ-effect of the iodine atom, as noted in [3], is small, and its individual components are also small (see Table 3); in this connection, it can be ignored in empirical analysis of $\delta^{13}C$ in monoiodoalkanes.

In Table 4 we show examples of the calculation of ^{13}C NMR chemical shifts for monoiodoalkanes that did not enter into the statistical material of (1) and (2). The deviations between the calculated and experimental values of the CS are no greater than the above-predicted error, ∿2 ppm. Since the structural increments for $\delta^{13}C_\alpha$ and $\delta^{13}C_\beta$ in total are greater than this error, we can state that the proposed additive scheme, i.e., Eqs. (1) and (2), is adequate in reliability of prediction of ^{13}C CSs in monoiodoalkanes.

The experimental material used in the present work does not furnish an adequate basis for judging the influence of branching at C_β and C_γ on $\delta^{13}C$ in monoiodoalkanes, although the ^{13}C NMR spectra of compounds (XIX) and (XXI) (Table 4) show that this influence cannot be very great.

EXPERIMENTAL

Of the compounds listed in Table 1 with a dagger (†), the 1-iodoalkanes were synthesized by halogen-exchange reactions [9]. The secondary iodoalkanes wre obtained by interaction of 1-alkenes with iodine or iodoform [10]. The ^{13}C NMR spectra were obtained on freshly distilled samples (60% solutions in $CHCl_3$) in a Bruker WP-200 SY Fourier-transform spectrometer at a frequency of 50.31 MHz with and without noise decoupling on protons, and also in the DEPT technique.

CONCLUSIONS

1. An additive increment scheme is proposed for the ^{13}C NMR chemical shifts in monoiodoalkanes with various types of structure.

2. The α-effect of iodine in monoiodoalkanes has a constant component that is equal to the α-effect of iodine in methyl iodide (the true α-effect); in addition, the α-effect depends on the number of carbon chains attached to C_α and on the total number of hydrogen atoms on all C_β.

3. The β-effect of iodine is determined to a considerable degree by steric interaction of iodine with protons at the particular C_β, and it is practically independent of the degree of branching of the molecule at the point C_α.

4. The ε-effect of iodine is 1 ppm or less, so that this effect and longer-range effects of iodine can be ignored in empirical evaluations of $\delta^{13}C$ in monoiodoalkanes.

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