

PROTON MAGNETIC RESONANCE STUDY OF THE CONFIGURATIONS OF SEVERAL β -SUBSTITUTED VINYL CARBONYL COMPOUNDS

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Teoreticheskaya i Eksperimental'naya Khimiya, Vol. 2, No. 6, pp. 757-765, 1966

PMR spectra of several β -substituted vinylcarbonyl compounds were studied. Analysis of the spin-spin interaction constants and the chemical shifts leads to the conclusion that the molecules of methyl *cis*- and *trans*- β -chlorovinyl ketone, methylmalondialdehyde, and malondialdehyde exist in a *cisoidal* conformation. The molecule of *cis*- β -chloroacrolein has a *transoidal* conformation, and a rotation around the C-C bond takes place in *trans*- β -chloroacrolein.

The results of the experiments are compared with calculated chemical shifts, which are determined by the effect of diamagnetic anisotropy and electrical charges of the C=C, C=O, and C-Cl bonds.

Many primarily IR and UV studies have been devoted to the problem of ascertaining the conformation with respect to the C-C bond in substituted 1,3-butadienes and β -substituted vinylcarbonyl compounds [1-4]. Recently, nuclear magnetic resonance has also been used for this purpose [5-8].

We studied high resolution PMR spectra of several β -substituted acroleins and of methyl β -chlorovinyl ketone. The results of the measurements are shown in Tables 1 and 2. Until now, the known isomers of β -chloroacrolein $\text{O}=\text{CH}-\text{CH}=\text{CHCl}$ (A) [9] and methyl β -chlorovinyl ketone $\text{O}=\text{C}(\text{CH}_3)-\text{CH}=\text{CHCl}$ (B) [10,4] have been assigned to the *trans* series on the basis of their chemical and physicochemical properties. Recently [11], the *cis*-isomers of these compounds have been obtained; their structure was confirmed by their chemical changes and their IR spectra. We obtained compounds A and B according to the method described in [11]. Malondialdehyde $\text{O}=\text{CH}-\text{CH}=\text{CHOH}$ (C) and methylmalondialdehyde $\text{O}=\text{CH}-\text{C}(\text{CH}_3)=\text{CHOH}$ (D) were obtained according to the methods described in [12] and [13].

Measurements of the spectra of A and B in the liquid state and in 50 mol. % CCl_4 solutions yielded identical results. The spectrum of C was measured in a 3 mol. % CDCl_3 solution containing about 1 mol. % ethanol. The spectrum of D was measured in a 3.5 mol. % CHCl_3 solution and in a 15 mol. % solution in carefully dehydrated acetone. Both measurements yielded identical results as far as the chemical shifts are concerned, but the CH and OH lines in the latter solution were broader. The acetone solution was prepared in a dry box containing dry argon, and the measuring cell with the sample was sealed. All solutions were prepared from freshly obtained materials, and all samples were kept at the temperature of dry ice until the measurement was made.

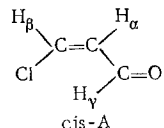
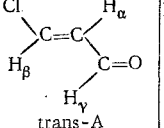
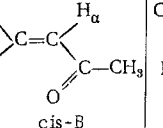
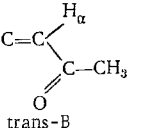
The PMR spectra were taken in a high resolution SYMR-62 spectrometer with a resolution of close to $4 \cdot 10^{-8}$ at a frequency of $\nu = 22.68$ MHz at a temperature of 22°C . The chemical shifts (ppm)

were measured with respect to cyclohexane as internal standard according to the lateral bands (around 15 mol. % of cyclohexane with respect to the compound studied). All δ values were recalculated in the δ -scale (with respect to $\text{Si}(\text{CH}_3)_4$ (TMS); toward the side of weak fields, δ for C_6H_{12} amounts to 1.43 ppm. The accuracy of the measurement was ± 0.05 ppm and the accuracy of the spin-spin interaction constants J was in the order of ± 0.5 Hz. The spectrum of the vinyl protons of methyl β -chlorovinyl ketone was calculated according to the scheme AB and the spectrum of β -chloroacrolein was calculated according to the scheme ABX with $J_{\text{AX}} = 0$ (X represents the aldehyde proton). The spectrum of malondialdehyde consists of a spectrum of the AB_2 -type (protons at the carbon atoms), which may be calculated in the first order, and of one peak of the OH proton. The spectrum of methylmalondialdehyde contains a line, corresponding to the signal from the two equivalent CH protons, the line of the methyl group in the strong field region, and the OH peak in the weak field region. The spectral data of A and B are given in Table 1 and those of C and D in Table 2.

Identification of the compounds under investigation by their PMR spectra showed that the pure *cis*-(A) and *trans*-(A) isomers of β -chloroacrolein, the pure *trans*-isomer (B) of methyl β -chlorovinyl ketone, and a mixture of 70% *cis*-(B) and 30% *trans*-methyl β -chlorovinyl ketone (see Table 1) were obtained in the synthesis. The *cis* form of A is completely converted into the *trans* form of A at 22°C within two hours.

The $J_{\alpha\beta}$ values (the interaction constants between α - and β -vinyl protons) for the *cis* and *trans* forms of A and B (Table 1) were found to be typical for the corresponding forms of similar compounds [6] so that they serve as basis for the identification of the isomers. The assignment of the lines in the PMR spectra was achieved on the basis of the spin-spin interaction constants of the H_γ and H_α protons (similar to the assignment in protonaldehyde [14] and also on the basis of the characteristic chemical shifts [15]. The spectral lines corresponding to the H_α protons in methyl β -chlorovinyl ketone are broadened, apparently because of a spin-spin interaction with the protons of the CH_3 group. The PMR spectra of the other compounds studied are also in agreement with their proposed structure. It has been shown previously that a *trans* as well as a *cis* conformation or a rotation around the C-C bond [1,2,6] may exist in substituted acroleins and vinyl

Table 1
Chemical Shifts δ (ppm) with Respect to TMS and the Spin-Spin Interaction Constants J (Hz) of the β -Chloroacrolein (A) and Methyl β -Chlorovinyl Ketone (B) Isomers

| Designation |  |  |  |  |
|--------------------|-----------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| δ_α | 6.31 | 6.44 | 6.44 | 6.44 |
| δ_β | 7.37 | 7.55 | 6.78 | 7.47 |
| δ_γ | 10.28 | 9.56 | — | — |
| δ_{CH_3} | — | — | 2.35 | 2.26 |
| $J_{\alpha\beta}$ | 7.6 | 13.6 | 8.1 | 14.0 |
| $J_{\alpha\gamma}$ | 7.7 | 6.9 | — | — |

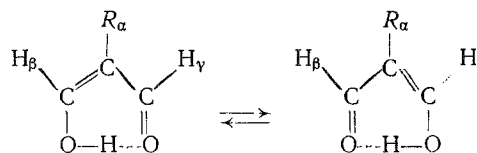
ketones. For the determination of the conformations in the compounds under investigation, we used experimental data on the J values and on the δ shifts.

An analysis of the spin-spin interaction constants between the protons for all conformations of mutual bond orientations of interest to us has been given in [6], namely: J_{cis}^s , J_{trans}^s , J_{cis}^d , J_{trans}^d in the cis and trans positions with respect to the single and double bonds. Starting from the assumption that the effects of the substituents on the J changes are additive, the following values were obtained for the hydroxy derivatives of the acroleins: $J_{trans}^d = 12.8$ Hz, $J_{cis}^d = 5.7$ Hz, $J_{trans}^s = 8.0$ Hz, $J_{cis}^s = 2.6$ Hz. Using in the analysis data for vinyl chloride given in [16] ($J_{trans}^d = 14.7$ Hz, $J_{cis}^d = 7.5$ Hz), we obtained, according to [6], the following values for the constants of β -chloroacroleins: $J_{trans}^d = 13.05$ Hz, $J_{cis}^d = 6.0$ Hz, $J_{trans}^s = 8.0$ Hz, $J_{cis}^s = 2.6$ Hz. Apparently, the assumption about the additivity of the changes in J due to changing the substituent is approximately satisfied. We measured directly the following constants for β -chloroacrolein: $J_{trans}^d = 13.6$, $J_{cis}^d = 7.6$; and for methyl β -chlorovinyl ketone: $J_{trans}^d = 14.0$, $J_{cis}^d = 8.1$ Hz (see Table 1). These values differ somewhat from the calculated ones. Apparently, these differences do not arise in the determination of the pure forms and in the evaluation of the content of forms which are converted into one another.

In the cis form of β -chloroacrolein $J_{\alpha\beta} = J^s = 7.7$

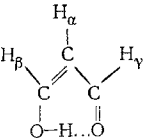
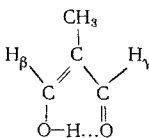
Hz, which is close to the calculated value of $J_{trans}^s = 8.0$ Hz. It follows that the cis-A form exists predominantly in the transoidal conformation. In the trans form of the same compound, $J_{\alpha\beta} = J^s = 6.9$ Hz, that is, based on the calculated data, the transitions between the transoidal and cisoidal conformations are faster so that the evaluation yields around 20% of the cisoidal conformation.

Malondialdehyde and methylmalondialdehyde are in the enol form and six-membered closed rings are formed from them with participation of a relatively stable hydrogen bond. Both are therefore in a cisoidal conformation with two rapidly interchanging tautomers:



(where $R_\alpha = H$ for C and CH_3 for D). This assertion arises from the following considerations. Above all, the chemical shifts of the OH group ($\delta_{OH} = 10.08$ ppm for malondialdehyde and $\delta_{OH} = 9.38$ ppm for methylmalondialdehyde) confirm the presence of an intramolecular hydrogen bond [17–19]. The existence of an intermolecular hydrogen bond is excluded because for methylmalondialdehyde the δ_{OH} values

Table 2
Chemical Shifts δ (ppm) with respect to TMS and the Spin-Spin Interaction Constants J (Hz) for Malondialdehydes (C) and Methylmalondialdehydes (D)

| designation |  |  |
|--------------------------------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|
| δ_{OH} | 10.08 | 9.39 |
| $\delta_\beta = \delta_\gamma$ | 8.48 | 8.36 |
| δ_α | 5.56 | — |
| δ_{CH_3} | — | 1.75 |
| $J_{\alpha\beta} = J_{\alpha\gamma}$ | 4.2 | — |

are identical in such different solvents as CHCl_3 and acetone (cf. [20]). Furthermore, the rapid transition between the above tautomeric forms indicates that no spin-spin interaction exists between the protons of the OH and CH groups [17]. Moreover, the β and γ protons are chemically equivalent and have a chemical shift of $\delta = 8.40$ ppm (Table 2), which is approximately equal to the mean of the shift of the proton in the $\text{C}=\text{C}$ double bond ($\delta \approx 7.30$ ppm) and of the shift of the aldehyde proton ($\delta \approx 9.5$ ppm) [15]. The same conclusion may be arrived at from an analysis of the $J_{\alpha\gamma}$ values. For the cisoidal conformation under rapid tautomeric exchange conditions

$$J_{\alpha\gamma} = \frac{1}{2} (J_{\text{cis}}^s + J_{\text{cis}}^d).$$

Substituting the calculated values of J_{cis}^s and J_{cis}^d for the hydroxy derivatives into this equation, we obtain $J_{\alpha\gamma} = 4.15$ Hz, which is in good agreement with experimental data (see Table 2). In [6], $J_{\alpha\gamma} = 9.69$ Hz was obtained for the same compound, which indicates the presence of an intermediate transoidal conformation. Apparently, this is due to the fact that in [6] the spectra of C were recorded in an acidic medium (water with HCl and other admixtures). This could have led to a proton exchange with the OH group, to cleavage of the intramolecular hydrogen bond, and to a change in the conformation of malondialdehyde.

Let us consider the chemical shifts in β -chlorovinyl carbonyl compounds. This analysis is particularly useful in the case of methyl β -chlorovinyl ketone and compounds similar to it, in which no H_γ proton is present. It is interesting also to compare the results independently obtained from an analysis of the J and δ values for other compounds.

An important factor is the considerable change in the chemical shifts of the protons during the transition from the cis to the trans form (Table 1). In our case, the chemical shift of the H_α protons toward weak fields increases somewhat during the transition from the cis to the trans form of A and is not changed during the transition from the cis to the trans form of B. The chemical shift of the aldehyde proton in A changes during this transition by 0.7 ppm. The signs of these changes are characteristic for the so-called cis effect [21], that is, the H_β lines in the spectra of the trans form lie in weaker fields than in the spectra of the cis forms; however, the H_γ and CH_3 lines lie in weaker fields in the spectra of the cis form.

It is known that for the previously studied substituted vinyl compounds, which have more steric hindrance and which have, however, substituents with a clearly defined polarity or diamagnetic anisotropy, the changes in δ_β during the transition from the cis to the trans form are considerably smaller than in our case (for instance, for α , β -dimethylethylene and many other compounds [20], this change does not exceed 0.1 ppm). For the compounds studied by us, the effect of steric hindrance on the

shifts of the vinyl protons is, apparently, also small. The values observed by us for the δ_β changes lie in a region which is typical for the cis effect in vinyl compounds containing functional groups of considerable anisotropy in the diamagnetic susceptibility or of considerable electric dipole moments (Table 3). In the compounds studied by us, such functional groups are Cl, $\text{C}=\text{O}$, $\text{C}=\text{C}$; in the cis transition the Cl atom affects all protons except the H_β proton, the $\text{C}=\text{O}$ bond affects all protons, except the H_γ proton (CH_3 in B), whereas the $\text{C}=\text{C}$ bond affects only the H_γ proton or the CH_3 group.

Let us consider the effect of the C—Cl bond specifically. Experimental data on the chemical shifts of chlorosubstituted olefins (e.g., from [15,16,20]) show that the change in the chemical shift of the H_α vinyl proton during the transition from the cis- to the trans-isomers is negligible (0.03 ppm). Apparently, our compounds are no exception to this. In fact, in methyl β -chlorovinyl ketone, the δ_α for both stereoisomers are identical within the experimental error (± 0.05 ppm, see Table 1). It may be assumed, for instance that in this case the effects of the magnetic anisotropy and the electric dipole moment of the C—Cl bond cancel one another for a given geometry of the molecule. The results shown make it possible to limit the effect of the C—Cl bond to δ_α . Concerning the effects of this bond on H_γ and CH_3 , we do not consider the number of experimental data in the literature to be sufficient. Starting from our results (Table 1), it may be assumed that this effect is significant.

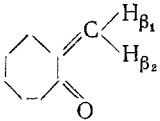
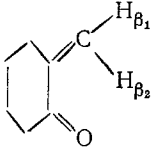
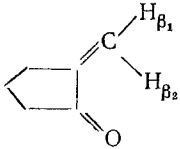
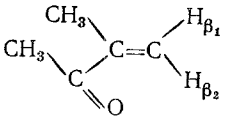
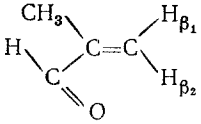
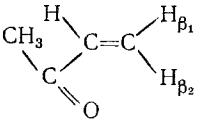
As follows from the available data (Table 3), the fundamental changes in the chemical shifts during isomer transitions* and the conformational changes must be attributed to the effect of the strongly polar $\text{C}=\text{O}$ bond for which a substantial diamagnetic anisotropy has been observed.

Attempts to base the conformational analysis of the isomers on the change in the proton chemical shifts during an isomer transition lead to the following results:

1. The absence of a change in δ_α during the isomer transition in methyl β -chlorovinyl ketone is in agreement with the assumption of an identical conformation with respect to the C—C bond in both isomers. The change in δ_α during the isomer transition in β -chloroacrolein may be connected with a conformational change and to a change in the bond angles. A qualitative consideration of the molecular geometry leads to the assumption that the effect of the change in the angles between the $\text{C}=\text{O}$ and C—H bonds or between the C—H and C—C bonds leads to a more significant change in δ_α in the case of the transoidal conformation. (The anisotropic and polar $\text{C}=\text{O}$ bond is in this case less far from H_α than in the case of the cisoidal conformation.) This is in

*We have in mind transitions from cis- to trans-isomers, which exist as individual compounds.

Table 3
 Effect of the C=O Bond on the Proton Chemical Shifts. The differences in the chemical shifts between two proton arrangements are given:
 $H\beta\Delta\delta\beta_2 = \delta\beta_2 - \delta\beta_1$. All results were taken from [5].

| Compound | $\Delta\delta_\beta$ | Remarks |
|-------------------------------------------------------------------------------------|----------------------|-----------------------------|
|  | 0.67 | rigid cisoidal conformation |
|  | 0.61 | rigid cisoidal conformation |
|  | 0.64 | rigid cisoidal conformation |
|  | 0.20 | flexible conformation |
|  | 0.27 | flexible conformation |
|  | 0.20 | flexible conformation |

agreement with the assumption that the transoidal conformation predominates in β -chloroacrolein.

2. The changes in δ_γ during the isomer transition may be due to an effect of the C—Cl bond and also (during the conformational change) of the C=C bond. When the possible changes in the O=C—H angle are taken into account, it must be admitted that a qualitative analysis of the changes in δ_γ may lead to opposite results.

3. A more direct approach to the conformational analysis of the compounds under consideration is provided by consideration of the change in the chemical shift of the H_β proton during the isomer transition. As is seen from Tables 3 and 4, the change in δ_β of methyl β -chlorovinyl ketone during the transition from one isomeric form to the other one coincides with the difference between the chemical shifts of β -vinyl protons in compounds with a rigid cisoidal conformation. This result indicates the presence of the cisoidal conformation in both isomers of methyl β -chlorovinyl ketone. The comparatively small change in δ_β during the isomer transition of β -chloroacrolein admits the assumption of only a small admixture of the cisoidal conformation in this compound, which is in agreement with the results of the $J_{\alpha\gamma}$ analysis and also with the magnitude of the change in δ_β of compounds with a flexible conformation (see Table 3.)

We calculated the contributions of the electric and magnetic effects of C—Cl, C=O, and C=C on the shifts of H_α , H_β , and H_γ for all possible planar configurations of molecules A and B. The results are shown in Table 4. We assumed that the electric and magnetic dipoles are localized at the Cl and O atoms, respectively, and at the center of the C=C bond. The bondlengths taken were: C—Cl 1.72 Å, C=O 1.29 Å (conjugated with the C=C bond), C—C 1.50 Å, C—H 1.05 Å, C=C 1.34 Å. (cf. [22]); the bond angles were taken to be constant (the H—C=C, H—C—Cl, and O=C—H angles are equal to 120°).

To evaluate the contribution of the electric field to the chemical shift in the calculated data (we assume that changes in δ with a positive sign correspond to changes toward strong fields), we used the Buckingham equation [23] with a Musher coefficient [24] (considering only the linear effect):

$$\delta \text{ (ppm)} \approx -2.9 \frac{p}{r^3} [3\cos(\widehat{pr})\cos(\widehat{zr}) - \cos^2(\widehat{pz})], \quad (1)$$

where p is the dipole moment of the substituent, z is a vector directed along the C—H bond, r is the radius vector of the proton under consideration in a coordinate system, the origin of which is at the dipole. In (1), p is expressed in Debye units and r in Å.

For the evaluation of the diamagnetic anisotropy contribution of the same substituent, we used the equation [25]

$$\delta \text{ (ppm)} \approx \frac{1}{3r^3} [\Delta\chi' (2 - 3\cos^2(\widehat{\mu r})) - \Delta\chi''], \quad (2)$$

where r is the radius vector of the proton under consideration and μ is a unit vector in the direction of the magnetic dipole moment of the substituent,

$$\Delta\chi' = \chi_{zz} - \chi_{xx}; \quad \Delta\chi'' = \chi_{zz} - \chi_{yy},$$

where χ_{zz} , χ_{yy} , χ_{xx} are the components of the diamagnetic susceptibility tensor in a coordinate system with the z axis, directed along the bond anisotropy (for instance C=O). The quantity $\Delta\chi$ in (2) is expressed in Å⁻³·10⁻⁶ and r in Å. We used the following values of the parameters for the determination of the effect of the magnetic anisotropic and electric dipole moments (the same values were used for A and B):

$$\begin{aligned} \text{for C=O: } p &= 2.9\text{D}; \Delta\chi' = -4.15; \Delta\chi'' = 11.0; \\ \text{for C=C: } \Delta\chi' &= 0.0; \Delta\chi'' = 9.7; \\ \text{for C—Cl: } p &= 1.5\text{D}; \Delta\chi' = +3.0; \Delta\chi'' = -1.0. \end{aligned}$$

The values of parameters $\Delta\chi$ for C=O were taken from [25] where, however, only the effect of the electric dipole of C=O was considered. The values of the parameters for the Cl atom were chosen in agreement with the assumption that the effect of C—Cl in vinyl compounds on δ_α is small (close to 0.03 ppm) during the isomer transition. Previously such evaluations for vinyl compounds have not been made. Table 4 shows the results of the calculation in terms of data on the changes of δ_α , δ_β , and δ_γ ; also given are the calculated values assumed for the isomers as functions of the different conformations, under the assumption of conformational equilibria, and experimental data.

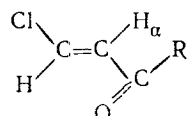
The calculated values of the change in the chemical shifts for H_β are in good agreement with the experimental data and with the assumption that the cisoidal conformation prevails in methyl cis and trans- β -chlorovinyl ketone, in cis-chloroacrolein the transoidal conformation, and in trans- β -chloroacrolein a mixture of the cisoidal conformation of the order of 28%, which is close to the value obtained from the conformational analysis based on the $J_{\alpha\gamma}$ values.

No such agreement is observed for the H_α and H_γ protons. For H_α , the opposite sign is obtained for the change in comparison with experimental data. When the angle between the C=O and C—H decreases by approximately 3°, the evaluation of the changing δ_α and δ_γ shows that δ_γ changes by 0.4 ppm. In the transoidal conformation, the same angular change may, because of the rotation of the C=O bond (we consider the remaining bond angles and bondlengths to be constant), lead to a shift of 0.1 ppm of the H_α line to strong fields. This assumption explains qualitatively the change in δ_α and δ_γ during the isomer transition in β -chloroacrolein. A similar change in the O=C—CH₃ angle in methyl β -chlorovinyl ketone cannot lead to a significant change in the shift of H_α (although the shift of CH₃ is changed) when the conformation of this compound is cisoidal.

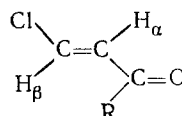
Table 4
Comparison of Calculated and Experimental Data on the Changes of Proton Chemical Shifts at H_α ($\Delta\delta_\alpha$), H_β ($\Delta\delta_\beta$), and H_γ ($\Delta\delta_\gamma$) During Isomer Transition as Functions of the Isomer Conformation (a + sign corresponds to a shift to strong fields). It is assumed that the atoms of all structures lie in one plane.

| Transition | $\Delta\delta_\alpha$ | $\Delta\delta_\beta$ | $\Delta\delta_\gamma$ |
|-----------------------------------------------------------------|-----------------------|----------------------|-----------------------|
| I \rightarrow III | -0.03 | -0.73 | 0.00 |
| II \rightarrow IV | -0.03 | +0.05 | +0.06 |
| I \rightarrow IV | +0.33 | -0.77 | +0.21 |
| II \rightarrow III | -0.39 | -0.09 | -0.17 |
| cis \rightarrow trans during conformational equilibrium | -0.03 | -0.41 | +0.02 |
| experiment (A) | -0.13 | -0.18 | +0.72 |
| cis \rightarrow trans experiment (B) | -0.00 | -0.69 | — |

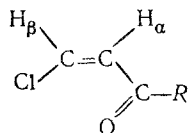
I trans-cisoidal



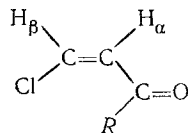
II trans-transoidal



III cis-cisoidal



IV cis-transoidal



where for A, $R = H_\gamma$,

for B, $R = CH_3$.

In this way all shifts observed by us can be qualitatively explained. It must, however, be pointed out that the use of the conventional dipole approximation [Eqs. (1) and (2)] may lead to incorrect results for the interaction between the H_γ proton with the C—Cl bond. Also, changes in δ are possible when intermolecular complexes are formed.

Consequently, it must be assumed that the transoidal conformation is far from being in all cases the only possible conformation of β -substituted vinyl-carbonyl compounds and that an essentially cisoidal conformation prevails in methyl β -chlorovinyl ketone, malondialdehyde, and methylmalondialdehyde. The intermediate conformation or rotation around the C—C bond in similar compounds may be determined by various factors. Among them are apparently weak steric hindrances (as, for instance, in methyl β -chlorovinyl ketone) and an intramolecular hydrogen bond (as in malondialdehydes).

It is obvious that the conformational analysis based on J values is more unambiguous than the analysis based on chemical shifts.

In all cases (ketones) when no H_γ (or H_α) proton exists in the molecule, the conformational analysis may be based on the chemical shift of the H_β proton, and, in the case of methylmalondialdehyde, it may be based on the shift of the OH proton. The assumption that the contribution of the Cl atom to the change in δ_α is small during isomer transition is extremely probable.

The authors thank N. M. Sergeev for his interest in their work.

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30 September 1965

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