Previous work [1, 2] described the addition of secondary and primary amines to vinylacetylene and \( \beta \)-alkoxyacetylene carbonyl compounds. The stereochemistry of the synthesized amino compounds was studied by the NMR method. The NMR data for some amino compounds are given in Table 1. From the spin–spin coupling constants (SSCC) \( J_{\beta H_2-H_\gamma} \) and \( J_{\gamma H_2-H_\delta} \), it follows that the dienic \( \delta \)-amino ketoesters (DAKE), \( \delta \)-amino ketones, and \( \delta \)-amino esters represent the trans-isomers at the \( \gamma, \delta \)-double bond, and exist predominantly in the form of the S-trans-conformers. On the basis of \( J_{\beta H_\alpha-H_\beta} = 15 \text{ Hz} \), compounds (V)-(VII) (see Table 1) were assigned to the trans-isomers at the \( \alpha, \beta \)-double bond.

The two sets of lines, observed in the spectra of (I)-(IV), could be assigned to the geometric isomers at the \( \alpha, \beta \)-double bond, as was proposed previously for the dienic DAKE [1]. The ratio between the isomers is equal to one.

A study of the DAKE by the NMR method at various temperatures disclosed that the DAKE, containing a secondary amino group [for example (I)], give additional lines in the spectrum of the protons at \( C_\gamma, C_\delta \), and \( CH_2 \) of the carbethoxy group when the temperature is lowered. The indicated change is not associated with tautomeric transformations, since a similar picture is also observed in the case of the compounds containing a tertiary amino group, which contains unsymmetrical substituents at the nitrogen atom. For the DAKE with a tertiary amino group, which has two identical substituents on the nitrogen, a nonequivalence in the chemical shifts of these substituents is observed when the temperature is lowered (0-20°). As a result, the reason for the changes observed in the NMR spectra is a hindering of the rotation around the C–N bond.

When the temperature was raised (0-150°) a broadening and merging of the lines, belonging to the isomers at the C–N bond, was observed initially as the result of an increase in the rotation rate around this bond. This was followed by a broadening and merging, and subsequent contraction, of the lines hypothetically assigned to the geometric isomers, in which connection the ratio between which did not change. On returning to the starting temperature the original appearance of the spectrum is restored. We briefly described this phenomenon in [3]. As an example, in Fig. 1 is shown the change in the spectrum of compound (II) when the temperature is raised. The mentioned averaging in the spectra, hypothetically assigned to the geometric isomers, should be related to an increase in the exchange rate between them due to the rapid (on the NMR time scale) rotation around the \( \alpha, \beta \)-double bond, observed under the equilibrium conditions. If the two sets of lines are assigned to the rotamers with an S-cis- and an S-trans-arrangement of the carbonyl and the \( \alpha, \beta \)-double bond, then the observed exchange must be explained by rotation around the \( C_\alpha-CO \) single bond.

The possibility of observing in the NMR spectra the separate rotamers, as well as the phenomenon of exchange between them as the result of rotation around the C–C single bond, is well known. However, several communications have appeared recently ([4], see also review [5]), which give some astonishing facts regarding rapid rotation around the C–C double bonds under equilibrium conditions, which was observed in the NMR spectra of the so-called topomers [5]. If the indicated rotation is observed in a temperature range that is standard for NMR spectrometers (−100 to −200°), then the value of the free activation energy \( (\Delta G^\circ) \) of such rotation does not exceed 23 kcal/mole [5]. In only one paper [6] were analogous
<table>
<thead>
<tr>
<th>Compound</th>
<th>X'</th>
<th>X'</th>
<th>X'</th>
<th>R'</th>
<th>cis-trans Isomers</th>
<th>Chemical shifts, ppm</th>
<th>Spin-spin coupling constants, Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
<td><img src="image.png" alt="Diagram" /></td>
</tr>
</tbody>
</table>

* cis-Isomers (I)-(IV) have a cis-arrangement of X' and H'.
* The chemical shifts are given on the δ scale.
* Due to its lability, the sample was taken at -23°C. At this temperature the lines of the δ, γ, and CH₂ protons undergo additional splitting, since the lines of each rotamer at the C-N bond are observed separately. A similar picture is observed in the spectrum of (III) at -23°C. The averaged chemical shifts based on these isomers are given.
* The chemical shift was determined approximately from the position of the lines of the methyl protons of the carbethoxy group. The chemical shift was determined approximately, and the SSCC was not determined because of the complicated nature of the spectrum of these protons due to the nonequivalence of the NCH₂ groups. Thermodynamically unstable. See text for details. The line of the NH proton is not observed separately due to the rapid exchange with the deuterium of the hydroxyl group of the solvent. (I) turns rapidly to a tar in other solvents. In the spectrum of (VII) in CCl₄ the NH line is observed in the 5.55 ppm region.