It is known that the cyclopropyl group promotes stabilization of carbocations, like vinyl or other unsaturated fragments [1-3]. There is no unanimity on the question of its effectiveness as a bridge group in the transmission of π-electronic effects. In a number of publications [3], the ability of the cyclopropyl and vinyl groups to participate in the interaction according to the mechanism of π conjugation is almost identical. Most of the results for substituted cyclopropanes, cited in [4], also agree with this concept. At the same time, more and more results of independent experimental [5-7] and theoretical [2, 8] investigations continue to appear, which cast doubts on the possibility of participation of the cyclopropyl group in the transmission of electronic effects according to a mechanism of σ-π conjugation.

In a study of cyclopropane and its derivatives by the methods of NMR spectroscopy, the above-mentioned contradiction is also manifested. Thus, the results of a measurement of the diamagnetic susceptibility and the shielding of 1H and 13C nuclei of unsubstituted cyclopropane are in good agreement, if we assume the existence in this molecule, analogously to aromatic rings, of an effect of a "ring current," due to 3.5 electrons, moving around a circle with radius 1.1 Å [9]. There is no theoretical explanation for such aromaticity. In a study of the 19F NMR spectra of 1,2-disubstituted fluorine-containing cyclopropanes [10], it was found that in ability to transmit π-electronic effects, they are only one fourth as effective as the ethylene analogs. Finally, a comparison of the changes in the chemical shifts (CS) of 13C in the series of substituted cyclopropanes and analogous derivatives of methane, ethylene, and benzene [11], the presence of a reliable linear relationship between the CS of the α-carbon atoms in cyclopropanes and the corresponding methane derivatives has been demonstrated. There is no relationship with the CS of vinyl and phenyl derivatives, which unquestionably casts doubts on the applicability of the model of σ-π conjugation in the series of cyclopropane derivatives.

In a study of the Raman spectra of cyclopropyl ethers [12], results were obtained, agreeing with the assumption of the presence of an effect of conjugation between the three-membered ring and the unsaturated groups, transmitted through the ether oxygen atom. A certain analogy in the chemical behavior of cyclopropyl ethers and their unsaturated vinyl analogs was noted earlier [13].

Below are discussed the results of an analysis of the 13C NMR spectra of a number of cyclopropyl ethers, which proved convenient for studying the question of σ-π interaction in substituted cyclopropanes. We studied the 13C NMR spectra of their vinyl analogs in detail and established the nature of the relationship of the parameters of the spectra and structural characteristics of the substituting groups [14].

Table 1 cites experimental values of the CS of 13C of a number of cyclopropyl ethers, as well as the CS of the α- and β-carbon atoms of the cyclopropane fragment, calculated.
according to an active scheme of calculation of sp³-hybridized ^{13}C nuclei in aliphatic compounds [15]. For comparison, the values of the CS of ^{13}C_α and ^{13}C_β of the double bond of the corresponding vinyl ethers are cited.

As can be seen from Table 1, the CS of ^{13}C_α and ^{13}C_β of the double bond undergo substantial changes, opposite in sign, from primary to tertiary alkyl substituents at the oxygen. The nature of the change in the CS of C_β in a first approximation, without considering the direct steric and anisotropic contributions, permits us to judge the degree of change of the electron density on it and is in good agreement with the model of steric inhibition of π-π conjugation by the substituent in vinyl ether derivatives [14].

The experimental and calculated values of the CS of ^{13}C of the cyclopropyl fragment are in good agreement quantitatively. An estimation of the degree of this interrelationship according to the method of least squares gives coefficients of correlation both for C_α and for C_β ~ 0.97, with a moderate dispersion (0.79 and 0.01, respectively). Considering the region of applicability of the additive scheme used for the calculation, we can conclude that the absolute values and the nature of the change in the CS of the carbon atoms in cyclopropyl esters are rather completely determined by the effects characteristic of derivatives of saturated hydrocarbons, i.e., do not require a consideration of such effects as the electron delocalization according to the mechanism of π-π conjugation.

A comparison of the nature of the changes in the CS of ^{13}C_α and ^{13}C_β in cyclopropyl and vinyl ethers reveals the far lower sensitivity of the CS of ^{13}C_β in the first case to the effects of the substituents. This is especially clearly manifested in a comparison of the changes in the CS of ^{13}C of cyclopropyl and vinyl derivatives, occurring when an ethoxy group changes to a vinyloxy group (see Table 1). In the first case the signal is shifted by 0.15 ppm in the weak-field direction, and in the second case by 7.02 ppm. The nature of such a substantial change in the series of vinyl derivatives is due to the mutual competition of the two vinyl groups for the unshared electron pairs of the ether oxygen according to the mechanism of π-π conjugation, which leads to a decrease in the electron density on C_β of each of them. In cyclopropyl ethers this change is almost 50 times smaller, which permits us to assume virtual absence of π-electronic interaction of the ring with the substituent.

Formally, the absence of an interrelationship between the nature of the changes in the CS of ^{13}C_β in cyclopropyl and vinyl ethers follows from the parameters of the correlation equations (Tables 2, 1 and 2).