A quantum-chemical investigation of the characteristics of the phosphorus-carbon bond and the internal rotation around it in phospha-alkenes has been carried out in the MNDO approximation. The results of the calculation have been compared with experimental dynamic $^1H$ NMR data.

The study of the nature of the multiple bond in compounds of two-coordinate phosphorus has been the subject of a number of theoretical investigations, which have mainly involved nonempirical calculations of the simplest compounds with a P=C bond, i.e., phospha-alkenes [1-3]. However, for methodological reasons, the greatest advances in the study of the electronic structure of real molecules are possible only on the basis of good nonempirical approximations. From the experimental point of view, the variation of the height of the barrier to hindered internal rotation as a function of the type of substituents at the phosphorus and carbon atoms may be an indication of an easily polarized $\pi$ component in the double bond. There have not hitherto been any data in the literature on any corresponding measurements.

We carried out a quantum-chemical investigation of the electronic structure of phospha-alkenes I-V (see Table 1) in the MNDO approximation [4]. The calculated barriers to rotation around the P=C bond were compared with the results obtained by the dynamic $^1H$ NMR method.

The height of the barrier to rotation was determined in the calculations as the difference between the total energies of the molecule in the initial configuration and after $90^\circ$ rotation of the carbon fragment around the P=C bond; complete optimization of the geometry of the molecule was carried out in both cases. The calculations were performed on an ES-1045 computer according to a program written by V. A. Zaits on the basis of the approach described in [4].
The rate constants of the process of hindered rotation were determined in the 303-470 K temperature range by means of a complete analysis of the line shape of the peaks of the dimethylamino and trimethylsilyl groups in the $^1$H NMR spectra, which were measured on Bruker HX-90 and WP-200 spectrometers according to the method described in [5]. The accuracy of maintenance of the temperature was ±0.2 K, and the accuracy of the determination of the value of the free energies of activation from the Eyring equation was ±0.8 kJ/mole.

The calculated lengths of the CH and CN bonds for compounds I-III are close to the experimental values [6, 7]. The bonds formed by the phosphorus and silicon atoms are 8-11 pm shorter than the experimental values, apparently reflecting the deficiencies of the parametrization of the third-row elements. For example, in the molecule of I $r(\text{PC}) = 156.6$ pm, while the experimental value is equal to 167 pm [6]. A similar picture was noted in the calculations of hydrides and oxides of phosphorus by the MNDO method in [8]. Nevertheless, the experimentally observed tendencies in the variation of the length of the P=C bond in phospha-alkenes under the influence of the substituents are correctly conveyed in our calculations: in molecule II the length of the bond is increased, and in molecules III-V it is diminished in comparison to the length of the bond in molecule I, in agreement with the tendency discovered for structurally similar molecules in the x-ray structural investigations in [7]. The bond angles and the tendencies for their variation are reproduced fairly well in the calculations. As an example, we present the data from the calculation of the geometry of molecule IV, which simulates the compound $\text{IP} = \text{C(SiMe}_3)_2$ (Si₁ and Si₂ are the silicon atoms in the cis and trans positions to the C₁ atom, respectively): $r(\text{P=C}) = 155.7$ pm, $r(\text{PCI}) = 198.9$ pm, $r(\text{CSi}_1) = 180.5$ pm, $r(\text{CSi}_2) = 181.2$ pm, $\angle \text{ClPC} = 109.5^\circ$, $\angle \text{PCSi}_1 = 130.0^\circ$, $\angle \text{PCSi}_2 = 114.9^\circ$. Molecules I and II, as well as the HPSCI₂ and CIPSiCI₂ fragments in molecules III and IV, are planar according to the calculation, in agreement with the data in [7]. In molecule V the nitrogen atom deviates 3.9° from the plane, and the amino group is turned 16° around the P-N bond. Such a configuration clearly does not prevent conjugation of the amino group with the P=C bond.

The results of the quantum-chemical calculations of molecules I-V are presented in Table 1. The distribution of the charges in molecule I corresponds to the data from the nonempirical calculations in [1, 2]. The addition of two amino groups to the carbon atom causes appreciable transfer of electron density to the phosphorus atom and the appearance of a negative charge on it. Conversely, in molecules III-V the π-acceptor effect of the silyl groups attached to the carbon atom causes additional displacement of the electron density from the phosphorus atom to the carbon atom and an increase in the negative charge on it in comparison to molecule I. We previously [9] obtained similar results in calculations carried out by the CNDO/2 method; they were interpreted as a manifestation of the conjugation of the lone pair of the amino nitrogen atom with the π system of the P=C bond, which is formed with considerable participation on the part of the phosphorus 3d AO. The results obtained in the present work with the use of the CNDO method support this conclusion. The inversion of the polarity of the P=C bond in compound II is manifested by a considerable change in the value of the chemical shift $\delta^{31}P$: the nucleus of the phosphorus atom is shielded to a greater degree in similar compounds than in other phospha-alkenes. For example, in the case of HP=C(NMe₂)₂, $\delta^{31}P = -62.0$ ppm [10], and in the case of CIP = C(SiMe₃)₂, $\delta^{31}P = +343.0$ ppm [11].

It follows from the calculated values of the bond indices and their π components that the π interaction is far less pronounced in the -N-P=C<system than in the P=C-N< system as a consequence of the small overlap of the orbital of the nitrogen lone pair with the π orbital of the adjacent atom. The interaction of the π component to the P=C bond with the lone pair of the chlorine atom and the effects of the σ, π conjugation with the silyl groups are apparently insignificant. These conclusions are confirmed by an analysis of the π orbitals of the molecules considered; the highest occupied and lowest occupied orbitals in all these compounds are assigned to the π type. The absence of appreciable conjugation of a two-coordinate phosphorus atom with the π system of a benzene ring was previously pointed out in [3]. It is apparently not only the result of the unfavorable configuration of the π-electronic orbitals of the corresponding molecular fragments, but also a consequence of the insignificant p character of the orbital of the phosphorus lone pair. In order to ascertain its hybridization state, we found the self-consistent hybrid orbitals of the phosphorus atom in molecules I-V. The transition to a basis of hybrid orbitals was realized by means of diagonalization of the atomic blocks of the density matrix by Jacobi's