The infrared absorption spectrum of γ-phenylpyridine has been recorded experimentally in the range 600-2000 cm⁻¹ and the fundamental frequencies and forms of the normal vibrations have been calculated using the valence force field. The experimental and calculated data show satisfactory agreement.

Among the heterocyclic compounds exhibiting high physiological activity, nitrogen-containing substances, many of which belong to the class of materials exhibiting analgesic action, are of particular interest. In recent years many derivatives of piperidine and pyridine have been prepared and their pharmacological properties have been studied. Many of the pyridine derivatives are of interest not only as medicinal products, but also as starting materials for the preparation of macromolecular compounds exhibiting valuable specific properties. Such compounds include, for example, vinylpyridine, which is prepared on the industrial scale. The study of the structure of these compounds is thus of considerable theoretical and practical interest.

Up to the present, only a small number of nitrogen-containing cyclic compounds have been studied by the methods of molecular spectroscopy. In particular, the absorption spectra of phenylpyridines have been insufficiently studied. There are only two papers on the absorption spectra of phenylpyridines in the near ultraviolet range of the spectrum. Gillam, Lambert, and Hey [1] showed that the phenylpyridine molecule can be regarded as planar, since the C-C bond between the pyridine and benzene rings is analogous in character to a double bond. Krumholz [2], in a paper devoted to a study of the ultraviolet absorption spectra of phenylpyridines and their derivatives, reached the same conclusion regarding the geometry of the phenylpyridine molecule.

There are no published data on the infrared absorption spectra of phenylpyridine. The present paper gives data on the infrared absorption spectra of γ-phenylpyridine and the results of a calculation of the in-plane vibrations of this molecule. carried out using the valence force scheme. (The γ-phenylpyridine was synthesized by Pkhalgumani under the direction of N. S. Prostakhov, whom the authors thank for providing the specimen.) Since interaction between the rings does not influence the out-of-plane vibrations (as established for the case of diphenyl), this type of vibration was not examined. The results of the calculation are compared with the experimental data. The spectrum of γ-phenylpyridine which we recorded was compared with the familiar spectra of benzene, pyridine, and diphenyl. The spectrum of γ-phenylpyridine shows a number of frequencies which are not present in the spectra of these three compounds. To interpret these frequencies, and also to establish the nature of the C-C bond between the rings and examine the interaction between the two rings, we calculated the fundamental frequencies and the forms of the normal vibrations, To confirm and refine these calculations we also calculated the partial derivatives of the frequencies with respect to the force constants.

Calculation of the coefficients of kinematic interaction. We assumed that the γ-phenylpyridine molecule is planar, like the diphenyl molecule [3]. Examination of the geometry of the γ-phenylpyridine molecule shows that it belongs to the symmetry type C₂ᵥ with a second-order axis of symmetry and a plane of symmetry. It can readily be shown that this molecule has 39 in-plane vibrations, of which 20 belong to the completely symmetric species A₁ and 19 to the antisymmetric species B₁. Dimensionless values for the bond lengths and atomic masses were used in the calculation.

The coefficients of kinematic interaction were calculated using the following values for the valence angles, bonds, and atomic masses:

for the benzene group [5]
reciprocal bond length ς_C-C = 0.7286,
valence angles ∠ C-C-C = 120° and ∠ C-C-H = 120°;
for the pyridine group [4]
reciprocal bond lengths ς_N-C₁ = 0.8044, ς_C₁-C₂ = 0.7910, ς_C₃-C₄ = 0.7802,
valence angles ∠ C₃N₄C₅ = 115°, ∠ NC₄C₅ = 125°, ∠ C₃C₄C₅ = 118°, ∠ C₄C₅C₆ = 118°,
∠ NC₅H₅ = 114°, ∠ C₅C₆H₆ = 120°, ∠ C₆C₅H₅ = 120°, ∠ C₄C₅H₅ = 121°.
The reciprocal atomic masses $\varepsilon_H = \frac{m_N}{m_H} = 1$, $\varepsilon_C = \frac{m_H}{m_C} = 0.0906$, $\varepsilon_N = \frac{m_H}{m_N} = 0.0777$.

The "spectroscopic" mass of the hydrogen atom $m_H = 1.098$ was taken as unit mass.

The length of the C–C bond between the rings was taken as 1.50 Å corresponding to the length of a single bond in paraffin molecules. Since the chief purpose of the calculation was to examine the nature of the C–C bond between the rings, the parameters defining the stretching vibrations of the C–H bonds were not taken into account, to reduce the order of the matrix and increase the accuracy of the calculation.

This procedure can be justified by the following considerations: the stretching vibrations of the C–H bonds cannot have a significant influence on the fundamental vibrations of the ring, because of the large mass of the carbon atom, which makes it possible to assume that the carbon atom does not move in the stretching vibrations of the C–H bond.

Another method for reducing the order of the matrix involved the use of additional relationships (a total of 17) between the natural coordinates of this molecule (the $\gamma$-phenylpyridine molecule has a total of 56 natural coordinates) [5, 6].

The coefficients of kinematic interaction were calculated using the formulas first proposed by M. A. El'yashevich [7].

Fig. 1. Model of the $\gamma$-phenylpyridine molecule

Selection of the force field. The calculations whose results are given in the present paper were based on the assumption that the force fields of the benzene and pyridine rings remain unchanged on formation of the phenylpyridine molecule. On the basis of this assumption, the values of the force constants for the benzene and pyridine molecules were taken from [5, 6].

A second assumption was that there is no force interaction between the benzene and pyridine rings, with the exception of the interactions of the angles $\theta_6$ and $\theta_7$ with the angles $\theta_1$ and $\theta_2$ (Fig. 1), for which the values of the dynamic coefficients were taken as $m_6 = 0.12 \times 10^6$ cm$^{-2}$, $m_7 = -0.02 \times 10^6$ cm$^{-2}$ [7].

The force constant characterizing the bond between the rings was taken as equal to $K_{C_4C_1} = 7.02 \times 10^6$ cm$^{-2}$. For the interaction between the angles $\theta_6\theta_6$, $\theta_7\theta_7$, $\theta_1\theta_1$, or $\theta_2\theta_2$, we took the value $K_\gamma = 0.90 \times 10^6$ cm$^{-2}$, calculated by G. B. Peregudov [8] for the diphenyl molecule.

The results of the calculation (characteristic frequencies and normalized values of the characteristic vectors), carried out on a "Strela" electronic computer using a program written by L. A. Grbiov, are given in Tables 1 and 2. These tables also give the values of the characteristic frequencies ($\nu_{\text{Obs}}$) obtained experimentally on a IKS-14 spectrometer (the spectra were recorded in KBr pellets with a NaCl prism). The absorption spectrum of $\gamma$-phenylpyridine is shown in Fig. 2.

From the discussion of the results below it follows that the interpretation of the spectrum obtained experimentally can be made much more complete by comparing the experimental and calculated data.

Discussion of results. It can be seen from Tables 1 and 2 that satisfactory agreement is observed between the experimental and calculated values of the characteristic frequencies. The mean discrepancy does not exceed 10–15 cm$^{-1}$, a discrepancy of 25 cm$^{-1}$ being observed only in a few cases.

Examination of the values of the characteristic frequencies shows that the 1599 and 1567 cm$^{-1}$ frequencies characterize the antisymmetric vibrations of the benzene and pyridine rings respectively. The in-plane bending vibrations of the C–H bond also play an important part in these vibrations.

Table 1, which contains data for the $A_1$ symmetry species, shows that the observed 1006 cm$^{-1}$ frequency corresponds to two calculated frequencies: 1024 cm$^{-1}$, relating to the benzene ring, and 1021 cm$^{-1}$, relating to the pyridine.