Compounds containing a phosphinimine group — P = N — are basic, and the strength of the basicity depends greatly on the nature of the substituents at the nitrogen atom. The basic properties are especially pronounced in N-alkyl(aryl)phosphinimines. Compounds of this type readily give crystalline salts with anhydrous hydrogen halides, and they react with alkyl and acyl halides. The basicity of this series of compounds has been evaluated quantitatively by potentiometric titration in nitromethane [1-4]. The pK_a (CH_3NO_2) obtained permit the investigated phosphinimines to be classed as strong organic bases; some of them are close in strength to triethylamine (pK_a 18.35) and diphenylguanidine (pK_a 17.20). The basicity of phosphinimines varied within broad limits (from 14.70 to 20.50), depending on the substituents at the phosphorus and nitrogen atoms.

We were interested in an investigation of the spectra of salts and complex compounds of phosphinimines in the course of a study of their basic properties. The interaction of phosphinimines with acids may lead to protonation of the molecule or to the formation of complexes with a hydrogen bond. It is known that during protonation phosphinimines add a proton to the nitrogen. The onium cation formed may have a phosphonium (A) or an ammonium (B) structure. The complex with a hydrogen bond can correspondingly be represented by structure (C)

\[
\begin{align*}
\text{(A)} & : \text{H} = \text{P} = \text{N} - \text{R} \\
\text{(B)} & : \text{H} - \text{P} = \text{N} - \text{R} \\
\text{(C)} & : \text{H} - \text{Ac}
\end{align*}
\]

Of course, structures (A) and (B) are limiting structures, and the onium charge can be delocalized in the PN group. However, the possibility remains that the distribution of charge may be close to one of the limiting structures, and this should find reflection in the vibrational frequencies of salts of phosphinimines. To elucidate this question, we studied the IR spectra of methyl halides (II) and the hydrobromide (III) of triphenylphosphine-N-phenylimine (C_6H_5P = N-C_6H_5 (I) and its complexes with phenol, p-bromophenol, and pentachlorophenol.

Triphenylphosphine-N-phenylimine and its Salts. In the spectrum of phosphinimine (Fig. 1a), an intense broad band is observed at 1350 cm\(^{-1}\), characteristic of the P = N bond [5]. When the hydrobromide [(C_6H_5)N=PNHC_6H_5]^+Br^- (III) is formed, this band disappears entirely (Fig. 1b); an intense band 975 cm\(^{-1}\) appears in the spectrum, which we assigned to the vibrations of the P-N bond of reduced multiplicity. Let us recall that the vibration of the P-N single bond should be expected in the region of 870-750 cm\(^{-1}\) [5, 6]. Calculations show [5] that this vibration is not characteristic of the P-N bond. Replacement of the hydrogen of NH by deuterium in the hydrobromide (III) leads to a weakening of the band 975 cm\(^{-1}\) and the appearance of a new band 895 cm\(^{-1}\) (Fig. 1c). Considering the noncharacteristic nature of the vibration of P-N, the observable shift after deuteration may indicate a relationship of the band 975 cm\(^{-1}\) to the vibration of the P-N bond, which support the assignments made above.
Analogous changes are observed in the spectra during the formation of methyl halides of the phosphinimine \((\text{C}_6\text{H}_5)_3\text{PN(CH}_3\text{)}_2\text{C}_6\text{H}_5\)⁺X⁻ (II) (Fig. 1e). The band of the \(\text{P}–\text{N}\) vibration here is observed at 915 cm⁻¹. The appearance of the band 1270 cm⁻¹ is apparently due to the vibration of the \(\text{N}–\text{CH}_3\) group [7]. This band is absent in the spectrum of the hydrobromide, while in the spectrum of the methiodide \((\text{C}_6\text{H}_5)_3\text{PN(C}_2\text{H}_5)\text{C}_6\text{H}_5\)⁻I⁻ it is shifted to 1230 cm⁻¹ [8].

The presence of a strongly shifted band of the vibration of the \(\text{P}–\text{N}\) group in the spectra of methyl halides (II) and the hydrobromide (III), the position of which approaches the band of the vibration of the \(\text{P}–\text{N}\) single bond permits us to consider that of the two possible extreme structures – phosphonium (A) and ammonium (B) – the former predominates to a substantial degree.

Also noteworthy is the absorption in the region of 2800 cm⁻¹, which is used as a spectral criterion permitting a judgment of the localization of the free pair of electrons of the nitrogen atom during the formation of ammonium salts [7, 9, 10]. The IR spectra of compounds with a \(\geq \text{N}–\text{CH}_3\) group have a band of medium intensity in the region of 2820–2780 cm⁻¹, which can be used for the spectral detection of these groups. The formation of ammonium salts associated with the participation of the free pair of electrons of nitrogen is accompanied by a disappearance of this band in the spectra of the salts. A band at 2830 cm⁻¹ is detected in the spectra of the methyl halides (II). This may indicate the presence of a \(\geq \text{N}–\text{CH}_3\) group in the molecule, with a free pair of electrons on the nitrogen atom, which in turn is evidence of a pronounced phosphonium structure of the salts.

A phosphonium structure of salts of phosphinimines also follows from the data of the NMR–\(\text{P}^{31}\) spectra. In the spectrum of the initial triphenylphosphine-N-phenylimine (I), the signal from the \(\text{P}^{31}\) nuclei at 17.5 ppm is displaced to −34 ppm when the hydrochloride is formed, i.e., into the region characteristic of the phosphonium phosphorus [11].

In addition, we should assume some delocalization of the free pair of electrons of nitrogen in the salts, which is indicated by the data in other regions of the spectrum. Thus, when salts of phosphinimine are formed, the characteristic changes in the intensities of the bands of the vibrations of the phenyl groups 1600, 1500, and 1440 cm⁻¹ are observed. It is known that these bands are sufficiently stable in their position, but their intensities vary within very broad limits [12]. For unconjugated structures, they are weak, and the band 1500 cm⁻¹ is more intense than the band 1600 cm⁻¹. The conjugation of the phenyl ring leads to a substantial increase in the intensity of the bands 1600 and 1500 cm⁻¹; moreover, the intensity of the band 1440 cm⁻¹ drops [12]. In the phosphinimine (I), the variation of the intensities of the bands 1600, 1500, and 1440 cm⁻¹ is characteristic of the phenyl ring in the conjugated state. When salts are formed, these characteristic spectral features disappear. Consequently, it can be stated that in salts of phosphinimine, the structure of the aniline type, in which the phenyl ring is conjugated with the free pair of electrons of nitrogen, is weakened.

In the spectrum of the hydrobromide (III), an extremely low value of the frequency of the valence vibrations of the \(\text{NH}\) group is observed. In the spectrum of a solid sample (see Fig. 1c), it lies in the region of 2650 cm⁻¹, while when the sample is dissolved in chloroform it is shifted to 2700 cm⁻¹ (Fig. 1d). Usually the absorption associated with vibration of the free \(\text{NH}\) groups is observed in the region of 3400 cm⁻¹ [12]. Therefore, the shift of this band to 2700 cm⁻¹ in the spectrum of the hydrobromide (III) should be attributed to the appearance of some positive charge on the nitrogen atom [13]. In the spectrum of the hydrobromide (III) in chloroform, together with the band 2700 cm⁻¹, an intense band appears at 2930 cm⁻¹, which the authors of [14] observed in the spectra of salts of triphenylphosphine-N-alkylamines \((\text{C}_6\text{H}_5)_3\text{PNHR}\)⁺X⁻ in chloroform solution. They assigned this band to the valence vibrations of the \(\text{NH}\) groups in the salts. It should be mentioned that a band of the same form and intensity is present in the spectra of solutions of methyl halides (II) in chloroform, where there are no \(\text{NH}\) groups. The use of deuterochloroform as the solvent shows that the band 2930 cm⁻¹ in the spectrum of the methiodide (Fig. 1f) disappears entirely, being replaced by a band at 2215 cm⁻¹.

These spectral data permit us to conclude that the band 2930 cm⁻¹, observed in the spectra of salts of phosphinimine in chloroform, is the shifted band 3024 cm⁻¹ of the vibrations of the \(\text{C}–\text{H}\) groups of chloroform, included in a hydrogen bond with the \(\text{Br}^-\) or \(\text{I}^-\) ions. Therefore, the assignment of the band 2930

*The spectra of the investigated methyl halides are identical. Figure 1 presents as an example only the spectrum of the methiodide.