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Vibrational spectra and internal rotation of chlorophosphines

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Abstract—The present paper is devoted to the investigation of i.r. spectra (400–4000 cm^{-1}) of $\text{ClCH}_2\text{PCl}_2$, $\text{C}_2\text{H}_5\text{PCl}_2$, $(\text{C}_2\text{H}_5)_2\text{PCl}$, $\text{Ph}(\text{C}_2\text{H}_5)\text{PCl}$ in gaseous, liquid and crystalline states and of Raman spectra of $\text{ClCH}_2\text{PCl}_2$ and $\text{C}_2\text{H}_5\text{PCl}_2$ in liquid state. The influence of temperature on i.r. spectra has been studied. The normal co-ordinate analysis of different conformers of CH_3PCl_2 , $\text{ClCH}_2\text{PCl}_2$ and $\text{C}_2\text{H}_5\text{PCl}_2$ has been carried out. The experimental material and normal co-ordinate analysis shows that in $\text{ClCH}_2\text{PCl}_2$, $\text{C}_2\text{H}_5\text{PCl}_2$ and $(\text{C}_2\text{H}_5)_2\text{PCl}$ the internal rotation around the P—C bond is possible and that these molecules are present in a liquid as a mixture of two rotational isomers. The terms V_k in the decomposition of potential energy of internal rotation into Fourier series has been evaluated in the approximation of the harmonic oscillator.

INTRODUCTION

The rotational isomerism and internal rotation in relatively simple phosphorus-containing molecules have been studied particularly by methods of vibrational spectroscopy [1]. However, the compounds containing 3-valent phosphorus have not yet been studied. The present paper is devoted to the investigation of the vibrational spectra and internal rotation in the series of chlorophosphines $\text{Cl}_2\text{PCH}_2\text{X}$ ($\text{X} = \text{H}, \text{CH}_3, \text{Cl}$), $\text{ClP}(\text{C}_2\text{H}_5)_2$ and $\text{ClPPhC}_2\text{H}_5$. The vibrational spectra of Cl_2PCH_3 and $\text{Cl}_2\text{PCH}_2\text{Cl}$ had been investigated before [2–4], and it was concluded that $\text{Cl}_2\text{PCH}_2\text{Cl}$ exists mainly in one conformation. But no theoretical analysis has been made and the experimental data concerning the spectra $\text{Cl}_2\text{PCH}_2\text{Cl}$ are incomplete. Besides, $\text{Cl}_2\text{PCH}_2\text{Cl}$ used in [4] contained a certain percentage of contaminations.

EXPERIMENTAL

The Raman spectra were obtained with a CODERG PHO spectrometer equipped with He–Ne laser. Infrared spectra were recorded in the frequency range 400–4000 cm^{-1} with a Karl Zeiss UR-20 spectrometer. For the investigation of the spectra at low temperatures a special cell cooled with liquid nitrogen was used. The principal construction of this cell is similar to those widely described in literature. All temperatures were recorded with a copper-constantan thermocouple, with a precision of $\pm 3^\circ$.

When investigating the i.r. spectra of crystals, the crystalline layer was obtained by cooling down a liquid film of the substance between the plates of KBr and NaCl. Crystallization was observed visually in crossed polaroids. To study the i.r. spectrum dichroism there was used a polarizer on the basis of transparent diffraction gratings [5]. While recording the spectra of the gas (saturated vapor) a 200 mm cell was used. The

conditions of the registration of these spectra changed in an optimal range in conformity with the problem under investigation. All the investigated compounds have been synthesized according to the methods proposed in [6–9].

RESULTS AND DISCUSSION

(1) $\text{ClCH}_2\text{PCl}_2$ —chloromethyldichlorophosphine

Some of the spectra are presented in Fig. 1 and Table 1. Spectra in the range of 600–800 cm^{-1} depend on temperature, state of aggregation and polarity of the medium. In transition from the gas to the liquid, a change in the relative intensity of spectral bands over the range of 752–780 cm^{-1} is observed (Fig. 1a, 1b). The relative intensity of 780 cm^{-1} spectral band in the spectrum of the solution of chloromethyldichlorophosphine in cyclohexane is greater, than that in the spectrum of the solution in acetonitrile. When cooling the liquid film down to approximately -130°C crystallization takes place, there is no 780 cm^{-1} band in the crystal spectrum (Fig. 1c). Though visual observation in the crossed polaroids undoubtedly shows crystallization of the sample, one cannot observe any notable dichroism of i.r. bands in the crystal spectrum.

The total combination of the experimental facts may be explained by assuming that the present compound is in the form of a mixture of the rotational isomers. 780 cm^{-1} band may be assigned to a conformation with a greater, and 752 cm^{-1} band—with a smaller dipole moment. A small redistribution of band intensities with a decrease in temperature may be explained by the proximity of ΔH to zero.