Continuing our investigation of the rotational isomerization of phosphoryl compounds [1, 2], we studied the influence of substituents at the phosphorus on the conformational equilibrium. It was reported in [1] that for methyl dimethylphosphinate, an equilibrium mixture of cis and skew forms is realized. In view of this, it seemed interesting to study the conformations of methyl phosphorodichloridate (MPDC), in the molecule of which the more electronegative chlorine atoms are at the phosphorus in place of methyl groups. In the literature there is a report that MPDC exists in the form of a mixture of at least two isomeric forms [3]. However, the authors made no attempt to assign the isomers to definite geometrical configurations. The isomerism of methyl phosphorodichloridothioate has been studied in detail by the method of IR spectroscopy [4].

We used two physical methods simultaneously for the identification of the isomers: IR spectroscopy and dipole moments, using the advantages of each of them according to the following scheme: 1. To establish the presence of dynamic equilibrium of the isomeric forms on the basis of the IR spectra and determine the relative amounts of the isomers in a nonpolar medium. 2. By comparing the experimental dipole moment with those calculated according to a vector scheme for various configurations, using the composition found from the IR spectra, to determine precisely what isomeric forms exist at equilibrium. 3. To assign the absorption bands in the IR spectra to concrete isomers.

Figure 1 presents the IR absorption spectra of MPDC in media of various polarity. The correlated variation of the intensities of the absorption lines 548, 607, 1027, 1300 cm⁻¹ permits them to be related to one isomer, which we shall denote isomer (I); the bands at 515, 580, 1060, and 1315 cm⁻¹ belong to the other isomer, (II). The clear dependence of the intensities of the absorption bands on the dielectric permeability of the solvents permits a determination of the ratio of the absolute integral intensities of the bands, due to the same vibrations of these isomers, according to the formula [4]

\[ \frac{S_{I}}{S_{M}} A_{I}^0 + \frac{S_{II}}{S_{M}} A_{II}^0 = 1, \]

where \( S_I \) and \( S_{II} \) are the areas under the contour of the band of a given vibration of the isomers (I) and (II), respectively.

Fig. 1. IR absorption spectra of methyl phosphorodichloridate at 293°K: 1) gas phase, \( p = 10^{-2} \) mm Hg; 2) n-hexane; 3) tetrachloroethylene; 4) chloroform; 5) acetonitrile; 6) liquid phase.
(II); $S_{st}$ is the area under the contour of the band which does not change its intensity during isomeric conversions; $A^0_1$ and $A^0_2$ are quantities related to the absolute integral intensities. To determine the ratio of $A^0_1$ and $A^0_2$, it is necessary to compile two equations, i.e., to determine the areas under the contours of the absorption bands in two media. We determined the areas of the bands at 607 [isomer (I)] and 579 cm$^{-1}$ [isomer (II)], belonging to $\nu_{as}$ PCl$_2$ in n-hexane and acetonitrile. The absorption at 1178 cm$^{-1}$ ($\gamma$-CH$_3$) was used as the reference band. The solution of the equations permitted a determination of the content of the isomers in media of different polarities (Table 1).

Estimating the maximum possible error in the determination of the areas due to overlapping of the bands at 25%, we assume that the isomeric composition was determined with an accuracy of $\pm 4\%$.

Using the temperature dependence of the intensities of the same absorption bands for a solution of MPDC in n-hexane and for the pure liquid, we determined the difference of the internal energies ($\Delta H$) of the isomers (I) and (II): n-hexane 170 $\pm$ 50 cal/mole, liquid phase 320 $\pm$ 50 cal/mole. Thus, a study of the IR spectra permits us to ascertain the presence of isomers of the investigated substance and to measure their energy difference.

The isomers were identified by the method of dipole moments. The experimental dipole moment ($\mu$) of MPDC in CCl$_4$ at 298 K is equal to 3.40 $\pm$ 0.03 D. The dipole moments of a number of the most probable conformations were calculated according to the vector scheme. The moments of the bonds were assumed equal to $\mu_{P-O} = 3.1$ D (the average between the moments of P = O in 4-methyl-2,6,7-trioxa-1-phosphabi
cyclo[2,2,2]octane 1-oxide [5] and phosphoryl chloride [6]), $\mu_{P-Cl} = 0.8$ D [2], $\mu_{O-P} = 0.6$ D [5], $\mu_{O-C} = 1.0$; $\mu_{CH_3} = 0.28$ D [1]. The valence angles were taken analogously to [1]. The conformation in which the $P=O$ and $O-C$ bonds lie in one plane was taken as the initial conformation ($\phi = 0$), when the moments of the bands were directed in the same direction. Table 2 presents the results of dipole moments for various conformations.

Substituting into the formula $\mu = \sqrt{\mu^2 + \mu^2 (1-x)}$ (where $\mu_1$ and $\mu_2$ are the dipole moments of the conformations (I) and (II); $\mu$ is the resultant dipole moment; $x$ is the content of the isomer (I)) the moments of the conformations (I) and (II), and using the ratio of the isomers in CCl$_4$, found from the IR spectra, we determined the resultant moments for all possible combinations of equilibria of the two isomeric forms (Table 3).

The best agreement with the experiment is observed for the equilibrium of 20% of the trans and 80% of the gauche forms. The discrepancy (0.3 D) between the calculated and experimental moments is also small for the equilibrium of 20% trans and 80% cis forms. The equilibrium of the forms with $\phi = 120^\circ$ (80%) and $\phi = 60^\circ$ (20%) is also sufficiently well suited. However, the conformations with shielding of uniformly directed $P-C$ and $O-C$ dipoles are relatively improbable. The equilibrium of 20% cis and 80% skew forms is also excluded, as a result of the fact that in a more polar medium, the more polar isomer should be stabilized, while in our case, when we go to acetonitrile solution, a decrease in the intensity of the bands associated with the isomer (I) is observed. The presence of the trans form

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O
/ |
/ | Cl
/ Cl
/ |
\ / CH₃
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is characteristic of the first two possible variations.