HYDROGEN BONDS AND ROTATIONAL ISOMERISM
OF \( \alpha \)- AND \( \beta \)-HYDROXYPHOSPHORYL COMPOUNDS

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The data on the spectral study of the structure of hydroxyphosphoryl compounds are ambiguous [1-3]. The purpose of this work was a comparative investigation of the intra- and intermolecular hydrogen bond in \( \alpha \)- and \( \beta \)-hydroxyphosphoryl compounds, according to the absorption bands of the basic vibrations of the hydroxyl groups \( \nu_{\text{OH}} \) in the IR spectra. We synthesized compounds (I) and (II), possessing \( \alpha \)-hydroxyls with respect to the \( \text{P}=\text{O} \) group and (III), (IV), possessing \( \beta \)-hydroxyls (Table 1).

In the spectra of the pure substances and their concentrated solutions in \( \text{CCl}_4 \), broad intense bands of the \( \text{OH} \) groups involved in an intermolecular hydrogen bond are observed - \( \nu_{\text{polymers}}^\text{P} \) [3]). As dilution with the solvent increases, shoulders that can be assigned to dimer associates [3] - \( \nu_{\text{OH}}^\text{d} \) - appear on the bands of the "polymers" on the higher-frequency side and grow. Subsequently, with decreasing concentration of the substances, the intensity of the bands of the "polymers" and "dimers" drops while at higher frequencies \( \nu_{\text{OH}} \) of the monomer molecules appear. The frequencies and relative intensities of the latter molecules do not depend on the degree of dilution. When \( C \leq 10^{-4} \text{ M} \), monomer molecules predominate in solution. The frequencies of the maxima of all the indicated formations are cited in Table 1. The interpretation of \( \nu_{\text{OH}} \) of the monomers for assignment to an intramolecular hydrogen bond was performed on the basis of a comparison of them with one another and with the data of [1-3].

According to this interpretation, monomer molecules of \( \alpha \)-hydroxyphosphoryl compounds exist chiefly in the form of an equilibrium of two types of conformers (the mutual orientation of the \( \text{P}=\text{O} \) and \( \text{C}-\text{O} \) bonds in the Newman projections is skewed [1]):

The conformational equilibrium in \( \alpha \)-hydroxy-compounds can be schematically depicted as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \nu_{\text{OH}}^\text{P} ) cm(^{-1} )</th>
<th>( \nu_{\text{OH}}^\text{d} ) cm(^{-1} )</th>
<th>( \nu_{\text{OH}} ) of monomers</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (\text{C}_2\text{H}_5\text{O})\text{P(O)CH}_2\text{OH} ) (I)</td>
<td>( \sim 3315 )</td>
<td>( \sim 3430 )</td>
<td>( \nu_{\text{OH}} ) free</td>
</tr>
<tr>
<td>( (\text{C}_2\text{H}_5\text{O})\text{CH}_2\text{P(O)CH}_2\text{OH} ) (II)</td>
<td>( \sim 3275 )</td>
<td>( \sim 3400 )</td>
<td>( \nu_{\text{OH}} ) free</td>
</tr>
<tr>
<td>( (\text{C}_2\text{H}_5\text{O})\text{P(O)CH}_2\text{CH}_2\text{OH} ) (III)</td>
<td>( \sim 3340 )</td>
<td>( \sim 3400 )</td>
<td>( \nu_{\text{OH}} ) free</td>
</tr>
<tr>
<td>( (\text{C}_2\text{H}_5\text{O})\text{C}_2\text{H}_4\text{P(O)CH}_2\text{OH} ) (IV)</td>
<td>( \sim 3330 )</td>
<td>( \sim 3400 )</td>
<td>( \nu_{\text{OH}} ) free</td>
</tr>
</tbody>
</table>

The most important for the substantiation of the correctness of the interpretation cited is the appearance in the spectra of \( \beta \)-hydroxyphosphoryl compounds of pronounced bands of the free hydroxyl \((\nu_{\text{free}}^{\text{OH}})\) (Fig. 1). The position of these bands is in full agreement with the frequency of the free primary alcohol group, taken in the literature [4], and there is no doubt of the interpretation. The absence, as a rule, of analogous bands in the spectra of \( \alpha \)-hydroxy-compounds (see [1, 3] and the spectrum of (I) in Fig. 1) can be explained by the entropy factor. In \( \beta \)-hydroxy-compounds, on account of the possibility of supplementary rotation around the C-C bond, the relative number of possible conformers without H-bonds is substantially higher. Moreover, evidently the large separation of the bands in their spectra also plays a role.

As a result of the clear identification of \( \nu_{\text{free}}^{\text{OH}} \), the assignment of all the other bands of the monomers in the spectra of (III) and (IV) [and by analogy, also (I) and (II)] to an intramolecular hydrogen bond with two possible proton acceptor centers in the molecules seems unambiguous. In the transition from (I) to (II) and from (III) to (IV), the frequencies \( \nu_{\text{OH}}^{\text{OH}}, \nu_{\text{dOH}}^{\text{dOH}} \) and \( \nu_{\text{free}}^{\text{OH}} \) decrease in agreement with the increasing basicity of the \( \text{PO} \) group. In this case the frequencies \( \nu_{\text{OH}}^{\text{OH}}, \nu_{\text{dOH}}^{\text{dOH}} \) and \( \nu_{\text{OH}}^{\text{free}} \) remain practically unchanged, which also corresponds to their assignment.

From the data cited it follows that an intramolecular hydrogen bond closing a six-membered ring (both with the phosphoryl and with the ester oxygen) in hydroxyphosphoryl compounds is stronger than that closing a five-membered ring. This series is similar to the order of the strength of intramolecular hydrogen bonds in diols and opposite to that proposed in [2]. In the latter study the proper degrees of dilution of the solutions were not reached, and the conclusions were based on the values of \( \nu_{\text{OH}} \) of "polymers," which are actually lower for (I) and (II) than for (III) and (IV). The absorption band of the "polymers" of \( \beta \)-hydroxy-compounds appears appreciably earlier, i.e., at lower dilutions than for \( \alpha \)-hydroxy substances (see Table 1). The greater strength of the intermolecular associations of (I) and (II) may be partially explained by the increased acidity of the \( \alpha \)-hydroxyl proton as a result of the inductive influence of the \( \text{PO} \) group. The latter effect evidently is also responsible for the decrease in \( \nu_{\text{OH}}^{\text{free}} \) for (II), although the reservation should be made that this band is observed only the form of a shoulder.

**EXPERIMENTAL METHOD**

The diethyl ester of \( \alpha \)-hydroxymethylphosphonic acid (I) and the ethyl ester of \( \alpha \)-hydroxymethylethylphosphinic acid (II) were produced according to the method of [6]. The diethyl ester of \( \beta \)-hydroxyethylphosphonic acid (III) was produced according to the method of [7]. The ethyl ester of \( \beta \)-hydroxyethylethylphosphinic acid, produced analogously to (III), had bp 88-89° (0.006 mm); \( c_{\text{D}}^{20} \) 1.4565; \( c_{\text{D}}^{20} \) 1.1027. Found: P 18.52; C 43.21; H 9.21%; MR 40.97. \( \text{C}_6\text{H}_{12}\text{O}_3\text{P} \). Calculated: P 18.65; C 43.33; H 9.03%; MR 41.17.

The IR spectra were taken on a UR-20 instrument at a rate of scanning 25 cm\(^{-1}\)/min, slit program 4. The calibration was verified according to the absorption spectrum of atmospheric moisture. During the process of the experiment, vessels with \( \text{P}_2\text{O}_5 \) were placed in the cuvette compartment to remove atmospheric moisture. The solutions were photographed in demountable cuvettes 146 mm long. An analogous cuvette with solvent was placed in the reference beam. The solvent was thoroughly dried and redistilled over \( \text{P}_2\text{O}_5 \). All the substances investigated were freshly prepared, after redistillation. The solutions were prepared directly before photography in a chamber filled with inert gas.

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