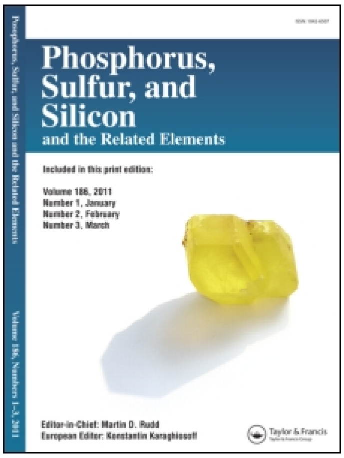

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The Structure of o-Hydroxyaryloxy-bis-(o-arylenedioxy)-phosphoranes and their Acid-Base Properties

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The Structure of o-Hydroxyaryloxy-bis-(o-arylenedioxy)-phosphoranes and their Acid-Base Properties

E.I.Matrosov*, D.I.Lobanov, N.V.Matrosova, M.I.Kabachnik
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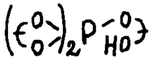
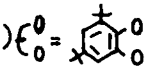
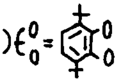
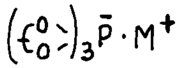
The crystalline phosphoranes  $\left(\{^{O}_{O}\rangle\right)_2P\langle^{O}_{HO}\}$ (I) a)  b)  have been obtained. IR-, UV- and NMR spectra of phosphoranes (Ia,b) and their interaction products with nitrogen bases have been investigated. It was determined that phosphoranes have structure (I) with pentacoordinate phosphorus and phenolic hydroxy group, while their products of interactions with nitrogen bases have the ionic structure (II) with hexacoordinate phosphorus  $\left(\{^{O}_{O}\rangle\right)_3\bar{P}\cdot M^+$ (II). The X-ray difraction approves the structure (I) for phosphorane Ib.

Acid-base properties of phosphoranes (Ia,b) were studied. New type of acid-base interactions was established. It was determined that in these compounds the proton transition is accompanied by the cyclisation. Therefore, the acidity of phosphoranes increases ($pK_a(CH_3NO_2)$=10,5); it is comparable with the acidity of substituted acetic acids. The neutralisation equation of phosphoranes can be presented in general form: $AH + B \rightleftharpoons {}^{*}A^- + HB^+$(1), where AH is phosphorane (I) (a weak pseudo acid), $^{*}A^-$ is phosphorate anion (II) (an anion of a true acid which existed only in its salts). In the case of strong bases the equilibrium (1) is completely shifted to the right, but in the case of the weak bases it is strongly dependent of the solvent.