H/D isotope effects on ^{1}H-NMR chemical Shifts in cyclic heterodimers and heterotrimers of phosphinic and phosphoric acids.

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Streszczenie

Hydrogen-bonded heterocomplexes formed by POOH-containing acids (diphenylphosphoric **1**, dimethylphosphoric **2**, diphenylphosphinic **3**, and dimethylphosphinic **4**) are studied by the low-temperature (100 K) ^{1}H-NMR and ^{31}P-NMR using liquefied gases CDF_3/CDF_2Cl as a solvent. Formation of cyclic dimers and cyclic trimers consisting of molecules of two different acids is confirmed by the analysis of vicinal H/D isotope effects (changes in the bridging proton chemical shift, δH, after the deuteration of a neighboring H-bond). Acids **1** and **4** (or **1** and **3**) form heterotrimers with very strong (short) H-bonds (δH ca. 17 ppm). While in the case of all heterotrimers the H-bonds are cyclically arranged head-to-tail, ···O=P–O–H···O=P–O–H···, and thus their cooperative coupling is expected, the signs of vicinal H/D isotope effects indicate an effective anticooperativity, presumably due to steric factors: when one of the H-bonds is elongated upon deuteration, the structure of the heterotrimer adjusts by shortening the neighboring hydrogen bonds. We also demonstrate the formation of cyclic tetramers: in the case of acids **1** and **4** the structure has alternating molecules of **1** and **4** in the cycle, while in case of acids **1** and **3** the cycle has two molecules of **1** followed by two molecules of **3**.

Słowa kluczowe

phosphinic acids, phosphoric acids, hydrogen bond, heterodimers, heterotrimers, heterotetramers, H/D isotope effects, NMR

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