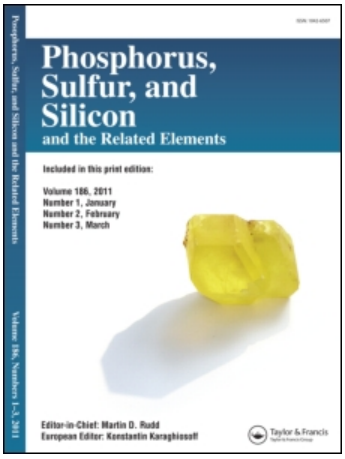

Phosphorus, Sulfur, and Silicon and the Related Elements

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New Synthetic Route to Phosphonic Acid Anhydrides

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NEW SYNTHETIC ROUTE TO PHOSPHONIC ACID ANHYDRIDES

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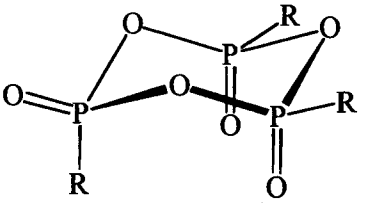
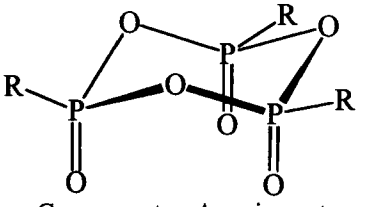
Phosphonic acid anhydrides are useful condensation reagents in the peptide and polyamide synthesis [1,2]. A new method for the preparation of well defined anhydrides is now described and intermediates of the peptide synthesis are elucidated. Cryoscopic and mass spectrometric data confirm the suggested cyclic trimeric molecular structure and the $^{31}P\{^{1}H\}$- as well as ^{1}H-NMR spectra can be explained with the structures:



C_s symmetry, AB_2 spin system;
R = 1,1 Dimethylethyl,
2-Methylphenyl



C_{3v} symmetry, A_3 spin system;
R = 2,4,6 -Trimethylphenyl

Reaction of t-BuP(O)$(SiMe_3)_2$ and $PhBCl_2$ yields the mixed anhydride of t-butylphosphonic and phenylboronic acid $C_{40}H_{57}B_4O_{12}P_4$. The compound forms colourless crystals and the obtained data are in agreement with a 16 membered P-O-B- ring.
By adding H_2O to a solution of the anhydride $[t\text{-}BuPO_2]_3$ [3] the hitherto unknown acid $H_2[t\text{-}Bu_3P_3O_7]$ can be obtained. This acid proved to be a strong acid and rather stable against further hydrolysis with H_2O in alcohohol. Neutralisation leads to the salt $[(t\text{-}Bu)_3P_3O_7]Na_2 * 8\ H_2O$, of which an x-ray structure was determined. Colourless, plate-like crystals; monoclinic, (a = 1086.9, b = 3113.9, c = 912.3 pm, b = 114.59°, $P2_1/c$, Z = 4, R1 = 0.040, wR2 = 0.119). The first of the two independent Na^+ cations is six-coordinated by five water molecules and one oxygen atom of the anion in the form of a distorted octahedra. The coordination of the other Na^+ ion by only five water molecules can best be described as largely distorted square pyramid with an Oxygen as apex. Both polyhedra share a common edge. The anions with their polar PO_2 groups and seven of the eight independent water molecules form hydrogen bonded layers perpendicular to b. Two such layers (equivalent across a centre of symmetry) are now connected to double layers by the eighth water molecule and the embedded Na^+ cations. This polar layer is „sandwich"-like enclosed in two nonpolar layers of t-butyl groups of the triphosphonate anions. Between those „sandwiches" only van der Waals interactions are observed.

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