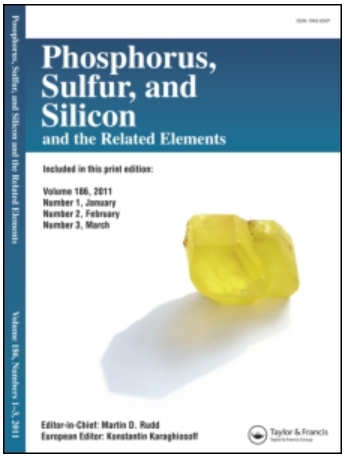

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Eight-Membered Phosphorus Heterocycles: Synthesis, Three-Dimensional Structure and Stereoelectronic Effects

R. P. Arshinova[a]; B. A. Arbuzov[a]
[a] A.M. Butlerov Research Chemical Institute of Kazan State University, Kazan, USSR

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EIGHT-MEMBERED PHOSPHORUS HETEROCYCLES: SYNTHESIS, THREE-DIMENSIONAL STRUCTURE AND STEREOELECTRONIC EFFECTS

R.P.ARSHINOVA and B.A.ARBUZOV
A.M.Butlerov Research Chemical Institute of Kazan State University, Lenin Str. 18, Kazan 420008, USSR

Abstract General conclusions on three-dimensional structure of 8-membered phosphorus rings are given in terms of the effects produced by the exo- and endocyclic heteroatoms, planar fragments, their number and localization. The role of anomeric effect in determination of exocyclic substituent orientation in 6-, 7- and 8-membered cycles is considered. The influence of stereoelectronic interactions in the conformational behavior as well as further prospects in this expanding field are discussed.

During the last decade enormous progress has been made in the chemistry of phosphorus-containing medium-sized rings, especially 8-membered heterocycles.[1] Among them there is a great variety of organic and inorganic, saturated rings possessing from one to four annulated aromatic cycles, and with a phosphorus atom in different coordination states, including their metallocomplexes. This chemical development promoted structural investigations. Structural phosphorus chemistry is of particular importance because it contributes to obtaining further information about the nature of chemical bonds, stereoelectronic effects, as well as about the reactivity and chemical behavior. The advances of conformational studies of phosphorus medium-sized rings are due to several causes: to the practical usefulness of compounds, to relatively simple synthetic access and to the fact that the theoretical background of conformational research has been developed earlier on the basis of the smaller rings.

This report is devoted to recent advances in the field of conformational analysis and electronic structure of various above-mentioned compounds with P^{III} and P^{IV}. In the first part general analysis of synthetic methods of the

considered heterocycles is given. Phosphorus chemistry affords wide possibilities in their synthesis starting with phosphacyclooctane containing only one P atom and finishing with fully inorganic cycles such as PS_7, P_4X_4 (X = N, Si, ...) and P_8. The variety can be extended by a large number of functional groups that can be developed around P centre and by introduction of annulated aromatic rings into different positions of 8-membered cycle. The reactions of phosphorus dihalides with dihydroxy-derivatives is a widely spread and relatively simple method of synthesis. The other opportunities include the use of dihalide derivatives of phosphorus acid ethers in dimerization reaction of 4-membered cycles or combination of smaller units. Different examples of such reactions are given.

The second and the third parts of the report are devoted to advances in conformational studies of saturated and unsaturated heterocycles. The analysis is based on the quantitative description of ring conformations which is given in terms of torsinal angles and puckering parameters.[2] This modern approach aliminates all ambiguities in identification of conformers. It represents all shapes of 8-membered ring by points on a five-dimensional hypersphere and permits to deduce the full set of canonical conformations. The introduction of heteroatoms into the ring considerably complicates this picture because their locations in the same conformations are not identical. Analysis and classification of a great number of 8-membered ring conformations are given on the basis of available X-ray structural data. In addition we carried out molecular mechanic calculations of 1,3,6,2-dioxazaphosphocines as models. The multi-dimensional maps of potential energy dependences from torsional angles are received and the most stable conformations are found. Local minima are consistent with 39 conformers, among them one BB and three BC as well as TBC (twist-boat-chair) conformers. Next ones in the energy scale are CC and TCC-shapes. These results produce the background for interpretation of experimental investiga-

tions and for generalization of all data.

The structural investigations for unsaturated dibenzo- and dinaphtho- annulated 8-membered compounds in solutions were promoted by the quantitative description and ^{1}H and ^{13}C NMR spectral criteria.[3] For some of three-component equilibria e-BC⇔B⇔a-BC of 4,5,7,8-dibenzo-1,3,2-dioxaphosphocine complex were found. Thermodynamic parameters for conformational processes of interconversion (~55 kJ/mol) and pseudorotation (~35 kJ/mol) are determined.

The inorganic unsaturated heterocycles with four planar fragments such as cyclotetraphosphazenes and some others are of special interest, because the comparison of conformational behavior of cyclooctatetraenes and inorganic phosphorus derivatives showed an essential difference: instead of boat-shaped the latter had CC, BB, butterfly or planar structures,[4] Special attention is paid to the conformational state of metallocomplexes with 8-membered ligands.

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