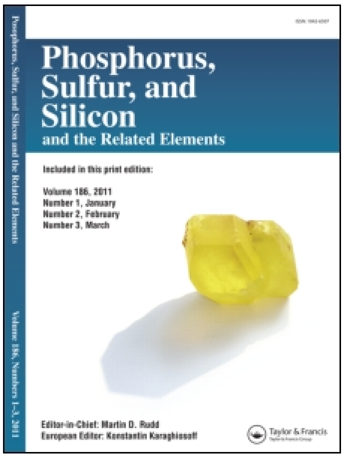

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Three-Dimensional Structure of P and B, N or S-Containing Six-Membered Heterocycles

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THREE-DIMENSIONAL STRUCTURE OF P AND B, N OR S-CONTAINING SIX-MEMBERED HETEROCYCLES

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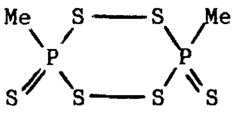
Abstract An analysis of conformational features of six-membered ring systems of the type of 1,3,5-diheterophosphorinanes with tri- and tetracoordinated phosphorus is given. Using IR, NMR spectra, dipole moments, as well as molecular mechanic calculation it was found the energy difference between chair and flexible shapes is not large enough, as in six-membered organic cycles, which causes participation of twist or boat in conformational equilibrium.

Conformational analysis of six-membered ring molecules has fascinated chemists for years.[1] Nevertheless, very little experimental and theoretical data exist concerning inorganic ring systems, especially about their conformational behavior in solutions. Conformational properties depend on the nature and mutual disposition of heteroatoms in the ring. In this paper we present some data on six-membered heterocycles, in which P^{III}(tri-) or P^{IV}(tetracoordinated)-atom is situated in 5-position in respect of two other 1,3-heteroatoms without exocyclic substituents (such as O,S or planar nitrogen in NR group), in other words, heterocycles of the type of 1,3,5-diheterophosphorinanes. Such a relative disposition of three heteroatoms in six-membered rings causes a significant reducing of 1,3-synaxial interactions for exocyclic substituents on phosphorus atom. That phenomena provides special conditions for "pure" manifestation of stereoelectronic effects which govern their three- dimensional structure. The same effect can be achieved by introducing of flat O_2BR-moiety. Pursuant to our current goal of analyzing the consequence of heteroatom's effects on ring conformations, we carried out the structural study of three types heterocycles with P,S- (1), P,B,O-(2,) and P,N- (3) atoms, which synthesis was described earlier.[3-5]



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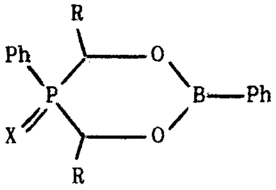

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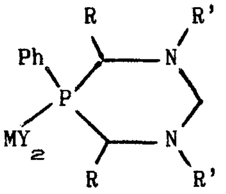
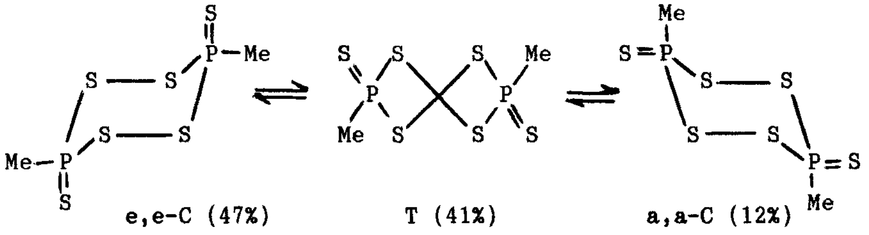


3

R=H,i-Pr,Ph,CCl_3; R'=Ph; X=LP(lone pair),S,Se

Besides proper cyclic systems (L), we were interesting in their complex derivatives. For experimental study we have used FTIR and NMR spectroscopy, dipole moments; the theoretical estimation of energy differences between conformers has been made by molecular mechanic calculations which had been developped for phosphorus compounds.[2]

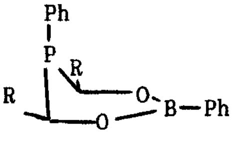
All systems posess exocyclic substituents. This feature causes the stereoisomery. For example, in species with exocyclic substituents around two cyclic atoms, as in system 1, two cis- and trans-isomers might exist; 1 can be consider as doubled 1,3,5- (or 1,3,2-)dithiaphosphorinane systems. Earlier both isomers were experimentally investigated.[3] We have perfomed MM-calculations. According to calculations, chair (C) and twist (T) shapes for six-membered rings are most stable. Trans-isomer can be characterized by tricomponent equilibrium:



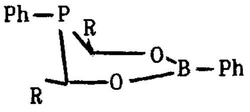
e,e-C (47%)   T (41%)   a,a-C (12%)

The energy difference between two alternative chair forms 0.8 kcal/mole, and between e,e-C and T-shapes 0.1 kcal/mole. In cis-isomer the presence of e,a-C (ΔE=0.4 kcal/mole,) and twist forms (ΔE=0.7 kcal/mole,) occur in the equilibrium of the type $a,e\text{-}C \rightleftharpoons T \rightleftharpoons e,a\text{-}C^{*}$. It results, that in 1,3,5-systems exocyclic substituents on P atom can easily change their orientation and even both chair shapes can participate in equilibration. The second conclusion consists of the nonsignificant energy difference between C and flexible shapes. That means that in polyheteroatomic systems flexible forms can be more probable than in organic cycles.

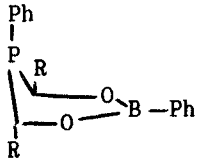
The important feature of 1,3,2,5-dioxaboraphosphorinanes with trivalent boron atom 2 is the plane disposition of five ring atoms C_2O_2B. In result six-membered ring can adopt only sofa (S) shape, in which the phosphorus atom is out of plane. In alkyl substituted 2 (R=i-Pr, Ph, CCl_3) in principle three stereoisomers can exist. All of them were observed for P^{III} species with R=i-Pr or Ph (the first symbol referred to the orientation of P-Ph group [4]):



a,e,e



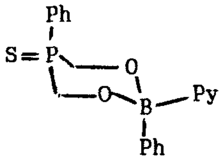
e,e,e



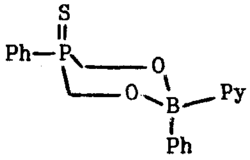
a,a,e

In the case of R=H when the fixing by stereoisomeric limitations is absent, the compound 2 (R=H, X=LP) exists in the equilibrium a-S$\rightleftarrows$e-S in the ratio 75:25. The same conclusion can be made for P^{IV} derivatives 2 with X=S,Se. From analysis of stereoisomer's dipole moments and nonequivalency of 4,6-protons it results that depending on reaction conditions only some of isomers might be isolated: if R=i-Pr, sulfide has a,e,e-S shape, while selenide - e,e,e-S; if R=Ph, both sulfide and selenide have a,a,e-S form.

In complexes 2 with piridinium (4) boron atom is a coordination centre, it changes its sp^2-hybridization to sp^3-one, and the six-membered cycle can adopt chair (or some flexible). All probable cyclic conformations were found using quantitative description on the basis of puckering parameters. The most interesting example concerns the structure of three individual stereoisomeric sulfides (X=S) with R=i-Pr. 4a and 4b have chair shape with different orientation of P substituents. As to third isomer,



4a a,a-C δ^{31}P 29ppm μ=5.90D



4b e,a-C 24ppm μ=4.28D

4c with δ^{31}P 50ppm, μ=5.55D, it has nonequivalent 4,6-protons, its polarity corresponds to nonsymmetrical B-2 or T-2 shapes. These data are very useful for study of such types of compounds. The identification of conformers showed, that usually sulfides or selenides with R=Me, i-Pr, Ph have one of this conformations. If R=H, the equilibrium between a,a-C and e,e-C is observed with the preference of first of them. It results, that complexation on boron atom provides the change of cyclic shapes, as to preference of substituent's orientation it retains.

Before study metal complexes 3 we investigated the conformational behavior of free ligand L. Changes in IR spectra revealed the dicomponent equilibrium a-C$\rightleftharpoons$e-C with predominating of the e-C. MM calculations proved this conclusion. So, the appearence of exocyclic substituents on 1,3- heteroatoms provides the reducing of a- preference of Ph-moiety on P-5. Complexation reactions L+M$\rightarrow$$L_2M$ were perfomed with M: $PtCl_2$(a), $PdCl_2$(b), $NiCl_2$(c), $CoCl_2$(d) and CuJ(e).[5] On the basis of vibrations analysis ν_s and ν_{as} (MCl_2) it was shown that complexes 5a-5c have cis-configuration with D_{2h} symmetry. Trans- configuration was proposed for black-coloured complex 5d, its green-coloured complex had cis or might be tetrahedral structure. The comparison of spectra for free ligand and complexes permit to make conclusion about the retaining of e-C conformation besides Ni-derivatives.

Concluding we can note that in 1,3,5-diheterophosphorinanes only in dioxa-systems the preference of axial orientation P-R bond manifestes (R=Ph). In 1,3,5-dithia- and diazaphosphorinanes this tendence is less pronounced. As to complexation, the main principles of conformational analysis for free ligands with six-membered heterocycles are usually well keeped in their complexes.

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