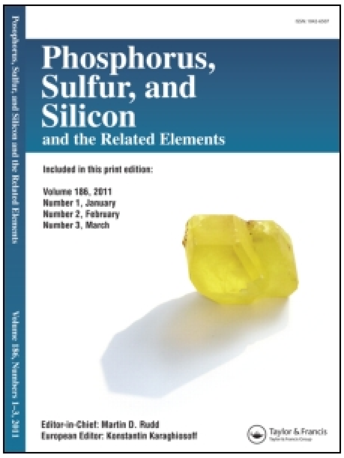

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Spatial Structure Heterocyclic Organoelement Compounds Determined by X-Ray Diffraction. Interpretation Model Based on Hyperconjugative Interactions

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. The interpretation model of the molecular geometry derived from X-ray diffraction data, which gives good results in the structures of symmetric 1,3,2-dioxa- and diaza-phosphacyclanes, is extended on the new classes of non-symmetric sterically hindered structures of 5,6-benzo-1,2-oxaphosphorines, 6,7-benzo-1,3,2- and 1,4,2-dioxa- and oxaza-phosphepines. It is shown, that steric ineractions may invert the anomeric effect of substituents. The observed changes of bond lengths are explained by electron density transfer as a result of hyperconjugative electronic interactions. The interpretation model is supported by the results of analysis of more than 30 structures.

Keywords: Stereoelectron interactions; anomeric effect; phosphaheterocycles; X-ray diffraction

INTRODUCTION

The theory of the hyperconjugative interactions was developed in the works of Deslogshamps, Roald Hoffman, and Epiotis with coauthors [1]. Most thouroughly it is written in the book of Kirby [2]. This model was also applied to interprete the structural features of phosphorus compounds by Arshinova, Mickolaijchyk [3]. This model was mainly used to interprete the orientation of substituents at the phosphorus atom, we consider it to be interesting to apply this model to consider the main geometrical parameters of phosphorus compounds.

We use these model for the medium size 1,3,2-dioxa- and 1,3,2-diazaphosphacyclanes (from 5- to 8-membered) [4]. This model is suitable not only to describe the bond length changes observed depending on the electron density transfer but also the difference of chemically equivalent bonds. The inversion of the anomeric interaction has

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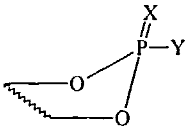
been observed due to steric hindrance leading to the opposite distribution of the geometrical parameters [5].

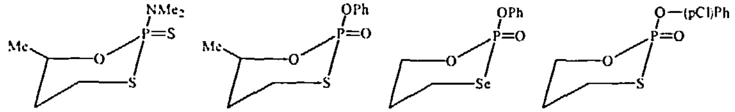


X = O, S, lone pair; Y = OR, NR_2, Aryl, Hal, Alkyl.

The aim of the present paper is to extend the model of hyperconjugative interactions to the structure of non-symmetric and sterically hindered molecules.

RESULTS AND DISCUSSION

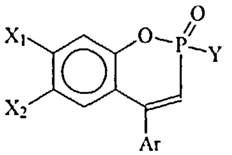
The first group of compounds we have studied includes the asymmetric 1,3,2-oxathia- and oxaselenaphosphorinanes:



1-4

The conformations of the heterocycles is chair, aryloxy-substituents at phosphorus being in axial position, the endocyclic P-O bonds in molecules **2-4** are shorter than those of exocyclic. Dimethylamino group in molecule **1** is in axial position, though there are no steric factors preventing it to adopt usual equatorial orientation. The P-N bond is elongated by 0.02 Å [6]. The conformation of aryloxy substituents is favourable for the hyperconjugative interaction of the oxygen lone electron pair with the antibonding orbital of the P-S (Se) bond. Obviously, low antibonding orbitals of the P-S (Se) bonds are more capable to interact with the oxygen lp than that of the P-O bond.

The next group of the compounds we have studied contains sterically strained unsaturated heterocycles – 5,6-benzo-1,2-oxaphosphorin-3-enes (10 structures).



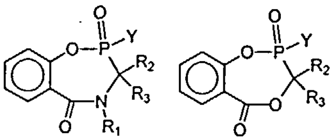
X_1=Cl,Br,H; X_2=Cl,Br,H
Y=O^-,OH,OMe,F,Morf.
Ar=Ph, p-Cl-Ph, p-Br-Ph
(5-15)

The conformation of these heterocycles is asymmetric boat: the P and C^3 atoms deviate from the plane of the rest 4 atoms [7]. In all molecules with oxygroups at the phosphorus atom they adopt axial orientation, as well as P-F bond, and the morpholine substituent is in equatorial postition. Thus the concept of anomeric interactions describe the orientation of substituents.. The values of the bond lengths are not easily interpreted in terms of anomeric effect as many factors influence these parameters. Among them; a large strain of the cycle, competition of the conjugation and hyperconjugative interactions, as well as strong intermolecular interactions in crystals:

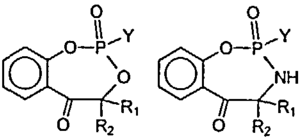
hydroxyl groups participate in hydrogen bonding. For ionic structures close distances between the cations and anions are observed. A notable elongation of axial P-F bond and an accompaning shortening of endocyclic P-O and P-C bonds are observed (in this crystal was not inermolecular interactions); the anomeric effect being responsible for these structural changes.

Thus for such heterocycles the concept of anomeric effect describes the orientation of the substituents at phosphorus but does not describe the tendencies observed in bond lengths in case of intermolecular interactions.

The next large group incudes unsaturated seven-membered heterocyclic compounds - 6,7-benzo-1,4,2-oxaza-, 1,4,2-dioxaphosphepines, 6,7-benzo-1,3,2-dioxa- and 1,3,2-oxazaphosphepines [8].



(16-28)



(29-35)

In these molecules two possible conformations are realized, both belonging to the family of distorted boats. The first type of conformations there is a planar fragment of 4 atoms condensed with the benzene ring, and P^2, $O^3(N^3)$ and C^4 are out of plain. In the second form, realised only for 1,3,2-dioxaphosphepines, there is a planar 5-membered fragment formed due to the conjugation of the carbonyl group with the benzene moiety, atoms P^2 and O^3 (N^3) are at one side of the plane. Of the structures **16-21** only 3 have oxygroup in pseudoequatorial position. The analysis of the bond lengths at phosphorus shows that as a rule pseudoaxial bonds are longer than endocyclic bonds. The exceptional are the structures with the hydroxyl group and anion structures. In molecules with pseudoequatorial orientation of the oxygroup the endocyclic P-O bonds are longer than exocyclic. These changes of the bond lengths may result from the reverse anomeric effect of the pseudoequatorial oxygroups.

For structures **29-35** an unexpected conclusion may be derived: the orientation of substituents can not be explained in terms of anomeric effect, however geometrical changes are in a good agreement with this concept. As in previous cases the changes in the ionic structures can not be explained in terms of stereoelectronic interactions.

CONCLUSIONS

On asymmetric 1,3,2-oxaheterophosphorinanes, asymmetrical 6- and 7-membered unsaturated cycles we can conclude the model of hyperconjugative stereoelectronic interactions satisfactorily describes the position of substituents at phosphorus. This model is also applicable to explain geometrical changes in the absence of strong intermolecular interactions — hydrogen bonds or anion-cation interactions.

EXPERIMENTAL

The X-ray single diffraction data for all compounds were measured on a "Enraf-Ninus" CAD-4 diffractometers using routine methods. The details of experiments and structural data will be published elsewhere.

ACKNOWLEDGEMENT

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