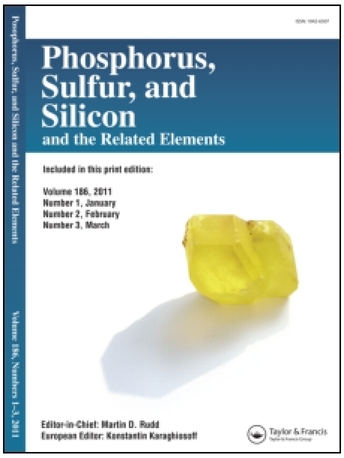

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INTRAMOLECULAR INTERACTION IN HETEROCYCLIC PHOSPHINES

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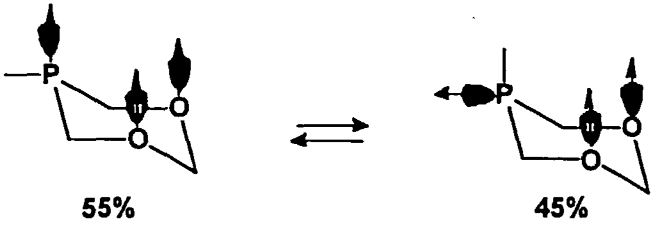
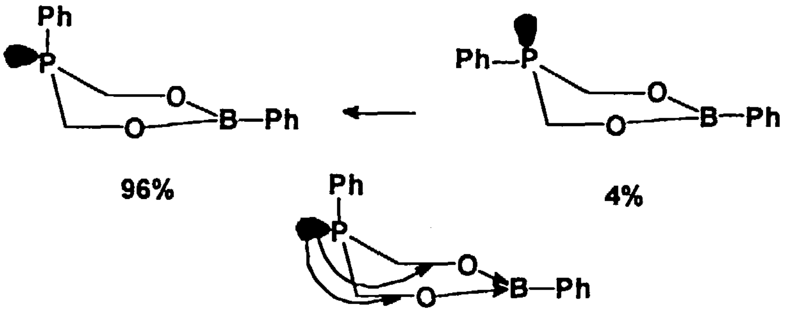
Some specific features of space structure, reactivity, complex formation and unusual physical properties of organic and organophosphorus compounds are due to univalent intramolecular interactions. Several intramolecular interactions observed in heterocyclic phosphines will be discussed in this current paper.

Heterocycles with the P-C-X fragments (X - heteroatom) are of interest regarding the interaction between phosphorus and the heteroatom and its influence on conformational behavior (substituent orientation, conformation of the ring, and inversion barriers). The quantity of conformers and stereoisomers of 1,3,5-dioxaphosphorinanes are in reasonably good agreement with dipole-dipole repulsion between lone electron pairs on phosphorus and oxygen. Moreover, the quantity of the conformer or stereoisomer with the axial orientation of substituents increases by substitutions of phosphorus lone pair on the oxygen, sulfur and selenium atoms. This correlates well with the increase of dipole-dipole repulsionion.

On the base of this theory the equlibrium of conformers of the 1,3,2,5-dioxaboraphosphorinanes the quantity of conformers with an axial orientation of the substituent on P-atom is bound to be smaller because the threecoordinated boron atom is a π-acceptor and the repulsion interaction must be smaller. However it has been found that the quantity of the conformer with an axial Ph group at the phosphorus atom is larger than in the above cases. This can be fairly well interpreted in terms of intramolecular donor-acceptor through-bond interactions (n-σ^*). In this case the electron density is transferred from the phosphorus atom to vacant orbital C-O bonds, which are activated by the boron atom.

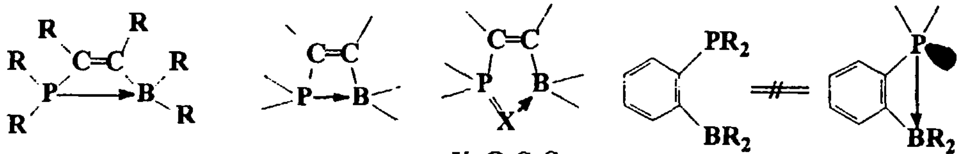


dipol-dipol interaction



n-σ* interaction

The next type of intramolecular interaction is a well known trans-annular donor-acceptor interaction. We are interested in compounds with P-C=C-B fragments. In these compounds the intramolecular trans-annular interaction are realised.

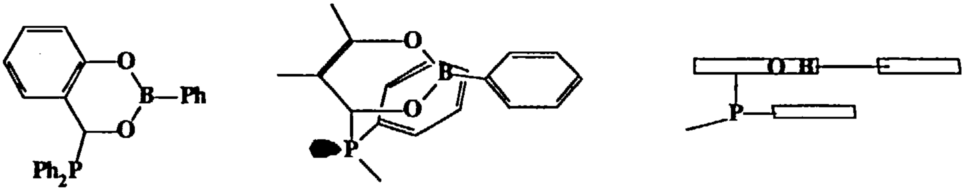


Binger P., Koster R.
J. Organomet. Chem.,
1974, 73, 205

X=O, S, Se

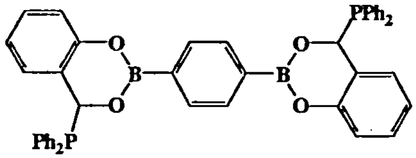
During the past several years we carried out systematic studies of the properties of Z-1,2-borylphosphinoethenes. We have demonstrated that the chemical shifts in ^{31}P NMR spectra, the dipole moments, and X-ray and mass spectral data all prove the existence of the P-B dative trans-annular intramolecular bond. The interaction in the oxides, sulfides and selenides is similar. In this case oxygen, sulfur and selenium atoms are donor centres. The o-borylphenylenphosphine is a structural analogue of borylphosphinoethenes. However it appears that the interactions between boron and phosphorus atoms are not observed in this system.

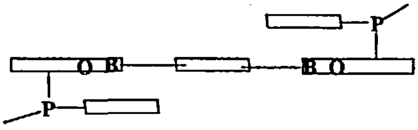
The dioxaborinanes with the exocyclic phosphine fragment were obtained by interaction of secondary phosphines, aromatic ortho-oxyaldehydes and boronic acid esters.



Dispersion Intramolecular Interaction
Overlapping stacks

However the properties of the compound that was obtained appeared to differ from those expected for compounds containing the P-C-O-B and P-C=C-B fragments. In contrast to these compounds, they exibit typical properties of tertiary phosphines and boronic acid, e.g. a high sensitivity to oxidation and hydrolysis, respectively. Parallel orientation of one of the phenyl substituents with the heterocyclic system should be mentioned, with short contacts (3.1 - 3.4 A) between the atoms of the phenyl ring and oxygen and boron atoms being observed in it crystal structure. Thus, there is no repulsion between the two planar fragments and the interaction between them are likely to result from dispersion forces. This is probably a first example of a "stacking interaction" of the cyclic boronic ester fragment. This interaction stabilizes the unusual conformation. The new substances were obtained from phenylendiboric acid with the aim to increase the number of interaction fragments. The properties of these compounds are analogous to properties listed above. In this case these may be a few structures in which stacking is available.



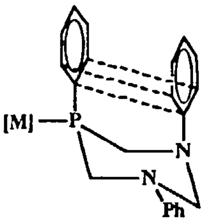


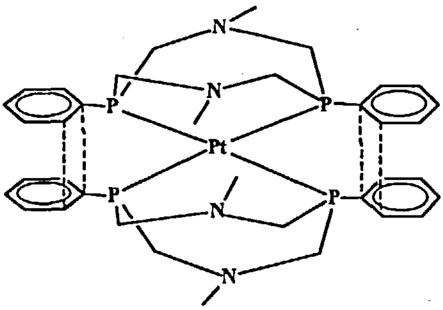
The planar nature of the dioxaborinane heterocyclic fragment determine the possibility of intramolecular interaction.

The computer simulations of 5-benzyl-1,3,2,5-dioxaboraphosphorinane shows, that the distance between the phenyl plane of axial benzyl group and O_2BC plane is equals nearles 3.2 A. The compound has been obtained in the crystal phase and was described by NMR and IR and Raman spectroscopy. This data have demonstrated that benzyl substitution have an axial orientation. There is reason to believe that staking takes place.

And finally a few words about the complexes of transiton metals with ligands which already possess a certain type of interactions. Intramolecular interactions may be observed in ligand, between the ligand fragment and the metal ion and between different ligands. For example, the six-membered ring ligands (1,3,5-diazaphosphorinane) possess a steric disadvantage conformation namely with two axial phenyl groups at phosphorus and nitrogen atoms, as shown for platinum and palladium complexes. Phenyl rings are parallel to one another and come within short distances of each other.

The stack between phenyl rings of two different ligands were observed in platinum(II) complexes of diazadiphosphacyclooctane.





The type of intramolecular interactions are far more numerous if works of other authers are taken into consideration.