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## Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

### Intramolecular Interactions of Phosphor-Containing Groups with an Aromatic Fragment in Different Conformations

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**To cite this Article** Ratovski, G. V. , Chwashev, D. D. , Sergienko, L. M. and Belaya, S. L.(1990) 'Intramolecular Interactions of Phosphor-Containing Groups with an Aromatic Fragment in Different Conformations', *Phosphorus, Sulfur, and Silicon and the Related Elements*, 51: 1, 242

**To link to this Article:** DOI: 10.1080/10426509008040776

**URL:** <http://dx.doi.org/10.1080/10426509008040776>

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## INTRAMOLECULAR INTERACTIONS OF PHOSPHOR-CONTAINING GROUPS WITH AN AROMATIC FRAGMENT IN DIFFERENT CONFORMATIONS

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Geometrical and electronic structure of conformers was studied by optical spectroscopy and quantum chemistry methods. The interaction mechanism of phosphor-containing groups with an aromatic fragment in  $YC_6H_4PX_2$  ( $Y = H, Cl, Me, OMe, NMe_2, C(O)OR$ ;  $X = Alk, OAlk, NAlk_2, Cl$ ) and  $YC_6H_4P(Z)X_2$  ( $Y = H, Cl, Me, OMe, NMe_2$ ;  $X = Alk, OAlk, NAlk_2, F, Cl$ ;  $Z = O, S$ ) compounds is discussed. In case of bisector conformation (A), where the benzene ring plane coincides with a  $XPX$ -angle bisectrix,  $\Pi$ -acceptor action of phosphorus-containing groups increases with  $X$  varying in a series:  $Alk < NAlk_2 \approx OAlk \leq F \ll Cl$ . These properties are displayed in ground and excited states of molecules, and are determined by interaction of  $PX_2$  and  $P(Z)X_2$  vacant group orbitals antisymmetric with respect to bisector plane with aromatic fragment  $\Pi$ -orbitals. For phosphorchloride groups  $\sigma$ - $\Pi$ -conjugation dominates and the  $d$ - $\Pi$ -conjugation contribution is small.  $\Pi$ -acceptor effect for  $P(O)X_2$  is weaker than for  $PX_2$  and  $P(S)X_2$  groups (especially in excited states) which is due to competitive transfer of electron density from oxygen to  $PX_2$  fragment. In case of the gonal conformation (B) where benzene ring and bisector plane of  $PX_2$  fragment are perpendicular,  $\Pi$ -donor effect of  $PAlk_2$  group is found to be 2-4 times weaker than for  $NAlk_2$ . According to quantum-chemical calculations with the MNDO method  $ArPX_2$  the stabilization of conformer B for  $ArPX_2$  increases in a series  $X: Cl \leftarrow C \equiv N < F < H < CH_3$ ; and for  $ArP(O)X_2$  the main conformation is (A).