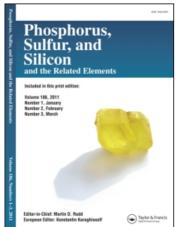
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Intramolecular Interactions of Phosphor-Containing Groups with an Aromatic Fragment in Different Conformations

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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(0)OR; X = Alk, OAlk, $NAlk_2$, Cl) and $YC_6H_4P(Z)X_2$ (Y = H, Cl, Me, OMe, NMe₂; 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, N-acceptor action of phosphorus-containing groups increases with X varying in a series: Alk < NAlk, \approx OAlk \leqslant F <<Cl. These properties are displayed in ground and excited states of molecules, and are determined by interaction of PX2 and P(Z)X2 vacant group orbitals antisymmetric with respect to bisector plane with aromatic fragment Π -orbitals. For phosphorchloride groups σ - Π -conjugation dominates and the d- Π -conjugation contribution is small. Π -acceptor effect for $P(0)X_2$ is weaker than for PX, and P(S)X, groups (especially in excited states) which is due to competitive transfer of electron density from oxygen to PX, fragment. In case of the gonal conformation (B) where benzene ring and bisector plane of PX, fragment are perpendicular, Π -donor effect of PAlk, group is found to be 2-4 times weaker than for NAlk, According to quantum-chemical calculations with the MNDO method ArPX, the stabilization of conformer B for ArPX, increases in a series X: $Cl \leftarrow C = N < F < H < CH_2$; and for $ArP(0)X_2$ the main conformation is (A).