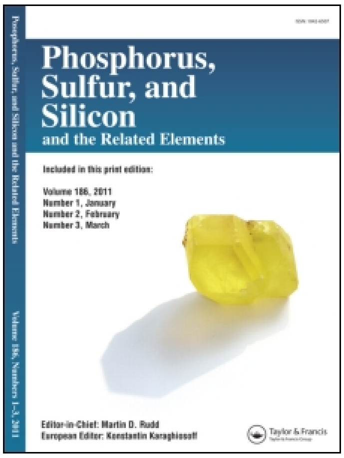

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Intramolecular Interactions of Phosphor-Containing Groups with an Aromatic Fragment in Different Conformations

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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(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, Π-acceptor action of phosphorus-containing groups increases with X varying in a series: $Alk < NAlk_2 \approx OAlk \lesssim F \ll Cl$. 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 Π-orbitals. For phosphorchloride groups σ-Π-conjugation dominates and the d-Π-conjugation contribution is small. Π-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, Π-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: $Cl \ll C{\equiv}N < F < H < CH_3$; and for $ArP(O)X_2$ the main conformation is (A).