ELECTRON TRANSFER IN PNICOGEN BOND

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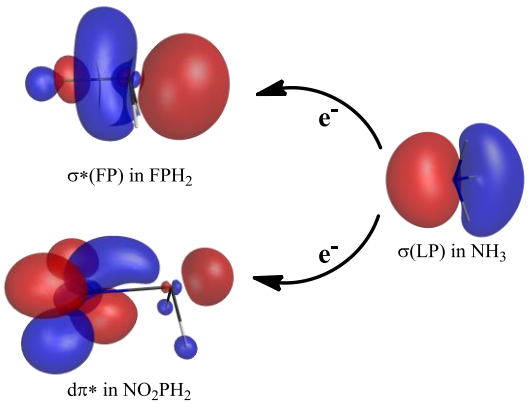
Western Michigan University, 2014



Non-covalent bonds and covalent bonds fall into two different categories in chemistry. Studies on non-covalent bonds were growing rapidly in the 20th century. Other than hydrogen bonds, many other kinds of non-covalent bonds have also been discovered and discussed. One of them is halogen bond, which is a non-covalent interaction between a halogen atom and a Lewis base. Similar to halogen bond, pnicogen bond is also a non-covalent interaction. In pnicogen-bond complex, pnicogen atoms (Group VA elements) act as Lewis acid, which can accept electrons from electron donor groups. In this research we applied the block-localized wave function method (BLW method) to the study of a series of substituted phosphines X_nPH_{3-n}. The advantage of BLW method is that it can define the electron localization state in monomers and complex, which means that electrons can be restricted in individual monomer. It makes the examination of charge transfer effect during the formation of a pnicogen bond feasible.

Also we have developed the orbital correlation diagram based on BLW, which helps us in identifying a new charge transfer pathway from the lone pair of NH_3 to phosphines. This charge transfer pathway is $n \rightarrow d\pi^*$. $d\pi^*$ orbital is formed by the interaction between d orbitals in pnicogen atom and π^* orbitals in nitro or cyano group. But for pnicogen bond, this explanation may still be oversimplified. The electron density difference (EDD) map shows that electron density only increases at one side of pnicogen atom, which is the σ-hole region.