

## MS32-P13 | EFFECT OF LOCALIZED NON-BONDING/REPULSIVE INTERACTIONS ON DISTRIBUTION OF ELECTRON DENSITY IN PI-CONJUGATED SYSTEMS

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Putting a local sterical pressure on conjugated pi-bonds can cause the electron density to flow away from the point where the pressure was applied onto less sterically hindered areas of the pi-system. Particularly, such in-plane inter-orbital repulsions are the origin of "Mills-Nixon effect" resulting in benzene rings with localized double bonds (Kekule's structure). An extensive analysis of both own and literature structural data reveals that short intramolecular contacts perpendicular to the plane of the benzene ring have the same effect. The list includes Kekule's structure formation in tripod arene metal pi-complexes along with some 1,3,5-substituted benzene cages and sterically overcrowded organic molecules. The examples of the out-of-plane contacts resulting in the pi-electron depletion for a sole pi-bond are much more numerous. The finding allows for intelligent engineering of pi-electron density distribution in electrophilic substrates.