CHAPTER 2

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CHAPTER 2

Structural Reorganization of Acceptor, BF$_3$

On Chemical Response

2.1 Equilibrium Structure of BF$_3$ and Its Reorganization of BF$_3$ on Chemical Response

At equilibrium ground state BF$_3$ molecule is a planar triangle with $\angle$FBF bond angles of 120$^\circ$. The planar BF$_3$ molecule possess the D$_{3h}$ point group at equilibrium state. This is predicted by VSEPR theory as the most stable shape for three outer electron pairs around any atom. The valence bond theory predicts that the central B atom is sp$^2$ hybridized at planar triangle geometry. The empty 2p$_z$ orbital on B atom is perpendicular to the triangle contains sp$^2$ hybrid orbitals. This empty p orbital may accept an electron pair from a filled p orbital of any one of three F atoms. Thus a dative $\pi$ bond is formed. If one localized double bond existed, then one of the three 'B–F' bonds becomes short whereas others are long. But different measurements show that all the 'B–F' bonds in BF$_3$ molecule are identical. The Valence bond explanation was the electronic structure of BF$_3$ is a resonance hybrid of three resonating structure with the double bond in different position [1].

Figure 2.1 Resonating structures of BF$_3$
2.2 Qualitative MO Picture

The 'B–F' bond lengths in BF$_3$ are 1.30 Å [1]. These bond lengths are significantly shorter than the sum of the covalent radii of B and F atoms (for B=0.80 Å and for F=0.72 Å). The 'B–F' bond energy is 646 kJ/mol, which is higher than any single bond energy. This shortening of 'B–F' bond is interpreted in terms of a π—π interaction. that is the 'B–F' bond in BF$_3$ posses some double bond character. The molecular orbital, MO theory, however, suggests then the double bond is fully delocalized. One empty p$_z$ orbital of B and three filled p$_z$ orbital from three F atoms form a four-centered π molecular orbital covering all four atoms. The empty 2p$_z$ orbital of B can accept lone pair of electrons from donor molecules like NH$_3$, Et$_2$O etc. only when the delocalized π bond is broken.

![Figure 2.2 π—π Overlap in BF$_3$](image)

2.3 Reorganization requires high activation energy

As B has an empty 2p$_z$ orbital in BF$_3$ molecule, it can accept a lone pair of electron in this orbital. So it should behave as Lewis acid [2]. According to Pearson’s [3] HSAB classification, BF$_3$ is a hard acid. This molecule is chemically very important and forms a large no of stable adducts with electron-pair donors (i.e. Lewis bases) [4]. When BF$_3$ molecule is in equilibrium planar form (D$_{3h}$), it is chemically almost inert [5,6]. An observed general structural characteristic of the BF$_3$ molecule in the donor-
acceptor adduct is that, BF₃ fragment assumes a pyramidal (C₃ᵥ) shape in the adduct super molecule. This proves BF₃ molecule undergoes a physical process of structural reorganization from planar (D₃h ) to pyramidal (C₃ᵥ ) shapes during the chemical event of donor-acceptor interaction. We can suggest a mechanism of structural reorganization expected in the instant case.

When a ligand, L begins to approach the BF₃ moiety along Z axis, the BF₃ molecule begins to deform quickly and reorganizes from its equilibrium planar form to pyramidal form. An examination of the chemical and physical characteristic shows that BF₃ is a very poor Lewis acid [7]. As the empty p-orbital of B atom form π-bond with filled 2p orbitals of F atom, the electron density on B-center increases and acidity of B-center decreases. Due to formation of π-π bond between B and F, ‘B–F’ bond possesses partial double bond character which is responsible for shorter bond length. When this molecule reorganizes from planar,D₃h (equilibrium form) to pyramidal(C₃ᵥ) form, the hybridization of central B atom changes and the π-π double bond is eliminated. So, the reorganization process of BF₃ involves two simultaneous and additive energetic effects-

(i) deformation of molecular structure and
(ii) the stretching of ‘B–F’ bond length along with elimination of partial double bond character.

So the reorganization energy of BF₃ molecule becomes considerably high. [8] because of the two conjoint action of bond stretching and π-bond breaking.
2.4 Symmetry Requirement of Structural Reorganization

It can be shown that if BF$_3$ molecule remains in planar form, the frontier molecular orbital, LUMO of BF$_3$ and the HOMO of donor systems do not match in symmetry types. Hence the overlap integral between the molecular orbitals involved in the physical process of charge transfer vanishes identically and the event of chemical reaction cannot occur between planar BF$_3$ and the donor molecules whose structural reorganization is either nil or insignificant. Hence in order to initiate and occur a chemical reaction between BF$_3$ and electron pair donor through a process of charge transfer, BF$_3$ molecule must undergo reorganization in spite of high reorganization energy.

2.5 Reorganization of BF$_3$ leads to its chemical activation

BF$_3$ molecule becomes hard and its Lewis acidity is poor because of its electronic structure as stated earlier. Though the molecule is intrinsically hard at equilibrium geometry, its property is significantly modified due to the physical process of structural evolution and the chemical reactivity of the molecule has high sensitivity toward the structural deformation. Ghosh et al [7,9] have studied the variation of chemical reactivity of BF$_3$ on structural reorganization in details in terms of molecular
orbitals, MO theory and density functional theory, DFT. The HOMO of the molecule is low lying and LUMO possesses high energy in equilibrium state. With the permission of authors, the plot of eigen values of LUMO and HOMO-LUMO gap as a function reaction coordinates are reproduced below. As the molecule begins to reorganize, the energy of LUMO decreases [9] at an accelerated rate. Thus the orbital receiving donation becomes progressively closer and closer to the HOMO of donor molecule and charge transfer interaction increases sharply.

Theoretical investigations revealed that the height of energy gap between HOMO and LUMO is an important stability index for molecules. Chattaraj [10] reviewed the
connection between the HOMO-LUMO gap and stability in various situations. The most stable electronic structure has the largest HOMO-LUMO energy gap. HOMO-LUMO gap of this molecule decreases with the structural reorganization i.e. the stability of BF$_3$ molecule decreases when it reorganizes from planer to pyramidal geometry. As a consequence, the BF$_3$ molecule becomes more reactive [9] due to reorganization. Hardness profile of this system follows the same trend as HOMO-LUMO gap i.e. hardness of BF$_3$ decreases when it reorganizes from planar to pyramidal form prior to the chemical reaction. Softness (inverse property of hardness) of BF$_3$ increases gradually during its reorganization.

![Plot of energy of HOMO-LUMO gap of BF$_3$ as a function of reaction coordinates](image)

**Figure 2.5**

*Necessary diagrams are reproduced here with the permission of the authors*

### 2.6 Present Work

As BF$_3$ becomes more reactive due to its structural reorganization, it forms many stable coordination complexes with different donors. We have, therefore, have
chosen BF₃ as acceptor unit in this study. The different donors selected here are NH₃, HCN, HNC, CH₃CN, CH₃NC. In this theoretical study, we want to investigate the formation, charge transfer and binding of

I. \[\text{BF}_3-\text{NH}_3\],

II. \[\text{BF}_3-\text{NC}\],

III. \[\text{BF}_3-\text{CN}\],

IV. \[\text{BF}_3-\text{NCCH}_3\],

V. \[\text{BF}_3-\text{CNCH}_3\] complexes.

Our main interest has been to investigate into the MO interactions during chemical interaction between the chosen acceptor and the donors. We are also interested to examine the correlation of chemical interactions between the systems in terms of descriptors of density functional theory. We shall try to analyze whether the instant chemical events of charge transfer follow some basic principle well known in conceptual chemistry- the chemical potential equalization principle and the maximum hardness principle, MHP. We want to further investigate whether the preferred site of reaction is consistent with the theoretical predictions in terms of local density functional descriptors.

This type of analysis will be helpful in understanding the basic features of chemical interactions viz. origin of charge transfer and bond formation between the two interacting systems.
References:


