

## **CHAPTER 8**

### *Conclusions*

This final chapter presents a comprehensive and a general conclusion of all the previous chapters. In the first chapter, a brief introduction to the origin and the chronological advancements of the concept of aromaticity through the course of history is extensively presented. The development of the theory of aromaticity and the advent of the synthesis of novel materials is discussed. A short summary of the different criteria for defining aromaticity based on energetic, magnetic and structural properties are described and the problem of unambiguously defining the concept of aromaticity is addressed. The concept of exo-cyclic aromaticity is introduced and how it has been an essential tool in stabilizing novel small ringed aromatic molecules is explored. Finally, the origin and development of the all-metal aromatic clusters are elaborated and the phenomenon of bond stretch isomerism that exists on a particular three membered all-metal aromatic cluster is analysed.

The second chapter provides an intricate detail of the different theoretical backgrounds that have been employed in defining aromaticity in this thesis. The quantification of aromaticity based on the chemical behavior, structural pattern, energetic and magnetic criteria is elaborately discussed. Aromaticity being a multidimensional phenomenon, the different indices of aromaticity that are utilized in this thesis to quantify aromaticity have been explained in detail. Since theoretical study of novel aromatic systems is the main objective of this thesis, so various theoretical indices that are employed in this thesis that could indicate the structural integrity of the proposed molecular systems are thoroughly elucidated. Finally, the theoretical background behind the popular global reactivity descriptors such as hardness, electrophilicity and electronegativity which give us an idea regarding the stability of molecular systems is explicitly discussed.

The third chapter offers a mini review of defining the concept of aromaticity in the light of magnetic criteria. Aromaticity is now no longer confined to the domain of organic chemistry and various inorganic clusters are found to be aromatic considering the delocalization of the electrons as the genesis of aromaticity. The ease with which aromaticity bridges the gap between traditional aspects of organic chemistry and latest discoveries in inorganic chemistry are truly fascinating. Aromaticity is not a physically observable quantity so defining it precisely is still a challenge. Quantification of aromaticity is a major challenge to the theoretical and the computational chemists till date. Whether aromaticity is a multidimensional phenomenon or it can be defined by a universal criterion is a debatable

topic. The journey of aromaticity from Kekulé's definition of benzene has been extensive and the recent developments in this field provide a considerable better insight into the concept. It is aptly said by Schleyer that, "aromaticity has been a time-dependent phenomenon." The perception of aromaticity is different in terms of its properties and characteristics to chemists with diverse backgrounds. The magnetic criterion for defining the concept of aromaticity has become very prominent surpassing the other criteria. Various developments in this field have occurred in the recent years and most of the developments were in the magnetic domain. So we can conclude by saying that the magnetic criterion is the most important criterion and provides a plethora of opportunities of future work on aromaticity.

The concept of exo-cyclic aromaticity in a novel aromatic molecule is introduced in chapter four. Aromatic cross-conjugated systems make it apparent that aromaticity must not be restricted only to the completely conjugated cyclic circuits. This inspires us to study a four-membered heteroatomic cyclic  $C_2B_2F_4$  molecule with  $D_{2h}$  symmetry which stretches the boundary of the concept of aromaticity by incorporating the idea of exo-cyclic aromaticity in the fourth chapter. In essence, the molecule  $C_2B_2F_4$  acquires aromaticity due to unusual participation of exo-cyclic atoms. Back donation of 4  $\pi$ -electrons from peripheral fluorine atoms to the electron-deficient boron atoms helps the ring to gain the magic number of 6  $\pi$ -electrons leading to a unique exo-cyclic aromaticity. Moreover, the existence of molecule with similar  $C_2B_2$  core makes us optimistic about the experimental realization of the molecule in near future.

The observation of unique aromaticity obtained through back donation of 4  $\pi$ -electrons from substituent exo-cyclic fluorine atoms to the vacant  $p_z$  orbitals of the boron atoms is further studied on proposed novel three-membered heterocyclic planar systems which are an interesting addition to the domain of aromaticity is studied in chapter five. Rigorous computational study involving DFT and *ab initio* calculations along with Energy Decomposition Analysis (EDA), the evaluation of Ring Strain Energy and HOMO-LUMO gap indicate towards the viability of the systems. The aromaticity of the molecule is evaluated through some standard criteria, specifically Nucleus Independent Chemical Shift (NICS) and Multi Centre bond Index (MCI). The dissected NICS analysis (CMO-NICS) presents a clear picture of the molecular orbitals contributing towards  $\sigma$  and  $\pi$  aromaticity respectively. A coherent picture of the exo-cyclic nature of the aromatic  $\pi$ -cloud is viewed with the AdNDP analysis. The Aromatic Stabilization Energy (ASE) based on a fully *ab initio* approach is also reported which renders the proposed heterocyclic molecules to be

remarkable 6  $\pi$ -aromatic systems where the *magic number* is attained through an 'exo-cyclic' conjugation. These proposed molecules are unique and distinctive due to the presence of both the  $\sigma$  and the  $\pi$  aromaticity and the antagonistic relationship existing between them makes the systems a remarkable addition to the class of aromatic molecules and provide a significant scope of future study. The high stability of the molecular systems as apparent from the various computational analysis makes us hopeful regarding the investigational reality of these molecules.

Comprehension of the inter-conversion between the bond stretch isomers of an all-metal aromatic  $\text{Be}_3^{2-}$  is unveiled in the sixth chapter. We illuminate the underlying rationale for the phenomenon of bond stretch isomerism in  $\text{Be}_3^{2-}$  and suggest that the Renner-Teller effect of the degenerate excited state linear intermediate is the main driving force behind the occurrence of bond stretch isomerism in  $\text{Be}_3^{2-}$ . The potential energy surfaces connecting different isomers through transition states and conical intersections are elucidated. Simulation based on ADMP method supports the fact of isomerization through the linear intermediate. Hardness and electrophilicity profiles also support the occurrence of Renner-Teller effect in this bond stretch isomerism. Stability ordering of the bond stretch isomers is in consonance with the calculated aromatic stabilization energy. Thus, as a whole this work provides an explanation to the intriguing phenomenon of bond stretch isomerism in  $\text{Be}_3^{2-}$ .

In the 7<sup>th</sup> chapter, the conceptual DFT based global and local reactivity parameters serve as an important chemical intuitive and predictive tool to elucidate the process of DNA modification i.e., the methylation of cytosine and its subsequent oxidation. Cytosine is one of the most essential DNA nucleobases which makes up the genetic code and its methylation is one of the widely studied DNA modifications. The following successive active demethylation pathway involving the iterative oxidation of 5-methylcytosine (5mC) to 5-(hydroxymethyl)cytosine (5hmC), 5-formylcytosine(5fC) and 5-carboxycytosine (5caC) is explained with the constructive methods of conceptual DFT based approach such as frontier molecular orbital study, chemical hardness and softness, local reactivity descriptors such as electrophilicity and nucleophilicity which provide considerable insight into the reaction pathway. Since the DNA nucleobases are aromatic molecules, aromaticity descriptor NICS also offers a significant understanding of the stability of cytosine and its derivatives as stability is intricately related to chemical reactivity.

So, this thesis provides a wholesome account of the concept of aromaticity including a review of the magnetic criteria for defining aromaticity. The concept of *exo-cyclic* aromaticity in novel molecular systems is introduced and is further established in novel three-membered heteroatomic aromatic systems. It explains the phenomenon of bond stretch isomerism in an important all-metal aromatic cluster. Finally, it provides theoretical elucidation of methylation of cytosine and its subsequent oxidation processes involving aromatic nucleobases.