ABSTRACT

The first chapter takes us in a journey of the concept of aromaticity since its inception days. The genesis of the concept of aromaticity, its chronological advancement, the problem with its proper quantification, the different criteria to quantify it and the lack of single unified criteria which makes it an important and relevant field of study is thoroughly discussed. The novel idea of exo-cyclic aromaticity is devised. The idea of aromaticity is extended beyond the domain of organic chemistry to all metal aromatic clusters and how bond stretch isomers plays an important role in these clusters is considered. Importance of aromaticity in DNA nucleobases is highlighted with reference to its biological applications.

The second chapter provides a concise description of the basic theoretical background related to the study of aromaticity. The discussion is centred on the various indices of quantification of aromaticity such as Nucleus Independent Chemical Shifts (NICS), Dissected Canonical Molecular Orbital NICS (CMO-NICS), Multi-centre indices, Electron Localization Function (ELF) and Aromatic Stabilization Energy (ASE) emphasizing on the significance of quantification of aromaticity. A brief background of the stability indices namely the Energy Decomposition Analysis (EDA), Ring Strain Energy (RSE), Adaptive Natural Density Partitioning (AdNDP) Analysis and Atom Centered Density Matrix Propagation (ADMP) is provided. The reactivity parameters involving the conceptual Density Functional Theory including both the global and local reactivity parameters (Fukui functions) are elaborately discussed.

In the third chapter, a mini review study regarding the most important criteria for defining aromaticity i.e., the magnetic criteria is comprehensively covered. Magnetic criteria of aromaticity have been analyzed which are currently the most popular methods, considering the circular delocalization of electrons as the genesis of aromaticity. The various magnetic measures for defining aromaticity such as NMR chemical shifts which include ^{1}H NMR shifts as well as Li^+ NMR chemical shifts, Magnetic Susceptibility Anisotropy, Current Density Analysis Plots (CDA) and Nucleus Independent Chemical Shifts are explicitly discussed. The NMR chemical shift is explained with the help of the Ring Current Model (RCM) and both experimental and computational applications are also discussed. Magnetic

Susceptibility Anisotropy and its applicability as a magnetic criterion have been elaborated accordingly. A pictorial representation of Current density Analysis Plots and its relevance as a magnetic criterion have also been accounted for. Special attention is given to the NICS criteria, explaining the role of ghost atom, considering it to be the most popular magnetic criterion. Advantages and disadvantages of all the methods along with recent advances are discussed.

The domain of aromaticity spans a wide range of molecules, from polycyclic aromatic hydrocarbons, heterocycles to all-metal systems. So, in the fourth chapter *in silico* we demonstrate the aromaticity in $C_2B_2F_4$, extending beyond the limit of conventional aromatic molecules. This molecule gains the magic number of six π-electrons through an unusual electronic contribution from *exo*-cyclic atoms. The stability of the molecule is established through density functional theory, *ab initio* calculations as well as molecular dynamics simulation.

In the fifth chapter, manifestation of exocyclic aromaticity is further established in novel heteroatomic molecular systems which demonstrate non-conventional aromaticity where the molecules accomplish the *aromatic sextet* and hence stabilization through the conjugation of *π*-electrons from the exo-cyclic substituents. A considerable σ-aromaticity is also observed which does not involve the exo-cyclic atoms. At first, the stability of these molecular systems is theoretically ascertained through various DFT and *ab initio* calculations along with the Energy Decomposition Analysis (EDA), T1 diagnostic run, estimation of Ring Strain Energy (RSE) and HOMO-LUMO gap which indicate towards the viability of these molecular systems. Then a detailed study of aromaticity with the aid of different computational probes such as Nucleus Independent Chemical Shift (NICS), Dissected canonical molecular orbital NICS (CMO-NICS) analysis, Multi Centre bond Index (MCI), Adaptive Natural Density Partitioning (AdNDP) and theoretical tool as Aromatic Stabilization Energy (ASE) based on a fully *ab initio* approach is performed which establishes unique exo-cyclic aromaticity in these systems.

In the sixth chapter, investigation of the underlying principle behind the occurrence of bond stretch isomerism in Be_3^{2-} is done. The various computational studies of the different isomers are carried out at complete active space self-consistent field (CASSCF) level of theory in addition to B3LYP level in conjunction with 6-311++G(d) basis set. The potential energy surfaces linking the different isomers through transition states and conical intersections are investigated at CASSCF level connecting various geometrical isomers of

Be_3^{2-}. The linear intermediate of the Be_3^{2-} cluster is considered to be of profound importance since its excited state is found to be degenerate and undergoing Renner-Teller effect producing two triangular bond stretch isomers. *Ab initio* molecular dynamics simulation based on Atom Centered Density Matrix Propagation (ADMP) method also further elucidates the phenomenon of isomerization via linear intermediate. The variation of the global reactivity descriptors and free energy profile along the bond stretch isomerization path is also investigated. Estimated aromatic stabilization energy also corroborates the stability ordering of the bond stretch isomers.

In the seventh chapter conceptual density functional theory involving the global and local reactivity parameters is employed to elucidate the process of methylation of aromatic nucleobase cytosine and its subsequent oxidation to its derivatives. The methylation of cytosine to 5-methylcytosine (5mC) is explained with the aid of condensed fukui functions. The active demethylation pathway following the iterative oxidation of 5-methylcytosine (5mC) to 5-(hydroxymethyl) cytosine (5hmC) to 5-formylcytosine (5fC) and finally to 5-carboxycytosine (5caC) is discussed with the help of conceptual density functional parameters such as Frontier Molecular Orbital (FMO) study, chemical hardness and softness, electrophilicity and nucleophilicity. Aromaticity of cytosine and its derivatives employing the Nucleus Independent Shift (NICS) is also employed to ascertain the stability which is in harmony with the hardness profile.

General conclusions of all the chapters are provided in the final chapter comprehensively focusing on the significance of the works done.